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A CHEMICAL STUDY OF RANCIDITY

II. FACTORS INFLUENCING THE KEEPING QUALITY OF SHORTENINGS AND CRACKERS[1]

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Introduction

The published literature contains numerous discussions of the effect of various storage conditions on the keeping qualities of butter and butterfat, but the data respecting like properties of other fats are rather scanty. The experiences of Emery and Henley (1922), Bevis (1923) and Greenbank and Holm (1924) may serve to indicate something of the behavior of edible fats when stored in contact with certain metals, and acids, and in light of varying intensity.

Since the keeping qualities of fats used in the production of soda crackers may be reflected in these properties of the crackers, it was anticipated that a study of the effect of various conditions of storage of commercial shortenings would be of interest to the cracker industry.

Effect of Different Conditions of Storage Upon the Keeping Qualities of All-Hydrogenated and Lard Shortenings

Five 6-pound cans of an all-hydrogenated shortening were received direct from the manufacturing plant. Two cans were immediately placed in a refrigerator at approximately 10° C., and the other three cans were stored in the laboratory. The keeping quality of these samples was followed through the storage period by the length of their induction periods when oxidized by the stirring method of Holm and Greenbank (1923). Odor, and Kreis (1902) tests were also made on the samples at the end of the experiment. The results of this experiment are reported in Tables I and II, while Table III gives the

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results of a similar study on the effect of various storage conditions upon a sample of open kettle rendered lard.

TABLE I

EFFECT OF AIR AND TEMPERATURE ON THE KEEPING QUALITIES OF ALL-HYDROGENATED SHORTENINGS ON STORAGE. KEEPING QUALITIES DENOTED BY THE LENGTHS OF INDUCTION PERIOD OF OXYGEN ABSORPTION FOR 200 GRAM SAMPLES OF SHORTENING OXIDIZED BY THE STIRRING METHOD AT 95° C.

Sample number	Time and condition of storage	Length of induction period of oxygen absorption
		Hours
1	Opened immediately upon receipt	6.25
2	Stored 7.5 months at 10° C.	6.00
3	Stored 16 months at 10° C.	6.00
2a	Stored 16 months at 10° C.; opened at the end of 7.5 months storage	4.50
4	Stored 2 months at room temperature	5.00
5	Stored 16 months at room temperature	6.25
1a	Stored 2 months at room temperature; opened at the beginning of the storage period	2.50
4a	Stored 7 months at room temperature; opened at the end of 2 months storage	1.50
4b	Stored 16 months at room temperature; opened at end of 2 months and 7 months storage	2.00

TABLE II

RELATIVE KEEPING QUALITIES OF A SHORTENING FROM DIFFERENT DEPTHS IN A CONTAINER

Sample number and storage conditions	Kreis test		Odor		
	Shortening in top layer of container	Shortening in bottom layer of container	Shortening in top layer of container	Shortening in bottom layer of container	Odor of entire sample
5—Stored 16 months at room temperature	Negative	Negative	Sweet	Sweet	Sweet
3—Stored 16 months at 10° C.	Negative	Negative	Sweet	Sweet	Sweet
2—Stored 16 months at 10° C., opened at end of 7.5 months storage	Very slightly positive	Negative	Sweet	Sweet	Sweet
4—Stored 16 months at room temperature opened at end of 2 and of 7 months storage	Very positive	Negative	Slightly rancid	Slightly rancid	Slightly rancid

TABLE III

EFFECT OF DIFFERENT STORAGE CONDITIONS ON THE KEEPING QUALITIES OF A LARD SHORTENING

Sample number	Storage conditions of the samples	Results obtained at the end of a year's storage	
		Kreis test on a 1-gram sample of lard	Odor of the melted sample
1	Stored in the laboratory	Strongly positive	Rancid
2	Stored in the laboratory	Strongly positive	Rancid
3	Stored at 10° C.	Slightly positive	Slightly rancid
4	Stored at 10° C.	Slightly positive	Slightly rancid
6	Stored in darkness in the laboratory	Strongly positive	Rancid
7	Stored in laboratory; 4 cc. water added	Strongly positive	Rancid
8	Stored in laboratory; 4 cc. water added	Strongly positive	Rancid
9	Stored 4 days in the laboratory, then at 10° C.	Slightly positive	Slightly rancid
10	Stored 4 days in the laboratory, then at 10° C.	Slightly positive	Slightly rancid
11	Stored in laboratory; air excluded	Negative	Sweet

Effect of Air on Keeping Quality.—The most striking results of this study is the effect of air on the length of induction period of oxygen absorption of the stored samples. All-hydrogenated shortening samples stored in unopened containers showed approximately the same length of induction period throughout their entire storage (Table I). Samples from containers once opened and then re-stored, all showed a decreased length of induction period when later subjected to this test. The lard sample (Table III) from which air was excluded, was to all appearances in as good a condition at the end of the year's storage as at the start of the experiment. Its length of induction period of oxygen absorption was 3.5 hours at the beginning and 3.0 hours at the end of the storage period as determined by the static oxidation method at 90° C. These results indicate the necessity of preventing undue exposure of the shortening to the atmosphere and of decreasing the amount of surface of the shortening exposed to the air.

Effect of Temperature on Keeping Quality.—The effect of temperature upon the keeping quality of the shortenings is clearly illustrated in Tables I, II and III. It is interesting to note, however, that samples stored at room temperature but without having had their containers opened to the air showed as long an induction period and exhibited as good an odor and Kreis test as those stored unopened in a refrigerator at 10° C. This indicates that for all practical purposes the presence of air is a necessity for the development of rancidity in shortenings, while an increase in temperature merely hastens the rancidity process. Storage of all-hydrogenated shortenings in a refrigerator at a low temperature, materially aids in inhibiting the

rancidity development as indicated by sample number 2 in Tables I and II. This shortening sample, although opened to the air at the end of 7½ months storage at 10° C., and then immediately replaced, did not show the same decrease in the length of induction period at the end of the 16 months storage as did those samples which were originally opened and stored at room temperature. Neither did this sample give the same rancid odor and positive Kreis test as the one stored at room temperature after opening. Similar results were obtained in the instance of the lard shortenings (Table III) when stored at room temperature. With the exception of sample 11, from which air was excluded, these were decidedly rancid. Lard samples stored at 10° C., for a year, were still in good enough condition to be used for edible purposes, although the Kreis test indicated that oxidation had proceeded to a considerable extent in them. Neither the absence of light, or the presence of moisture appeared to exert any appreciable effect upon the keeping qualities of these lard shortenings when stored for a year.

All-hydrogenated shortening samples 2 and 4 in Table II indicate that the upper layer of the solid shortening in a container, being in contact with the air, may be in a different stage of rancidity development than the shortening directly beneath it. It is evident in samples 2 and 4, which were from containers opened and then re-stored, that both had rancidity development farther advanced in the top layers exposed to the air than in the rest of the sample. While the entire shortening sample number 4 had acquired a rancid odor, this was due largely to the absorption of the odor in all probability, rather than to rancidity development in the whole sample, since the Kreis test was negative except in the upper layer.

Relation of the Chemical Characteristics of Shortenings to Their Keeping Quality

Free Fatty Acid Content versus Keeping Quality. The free fatty acid content of a fat represents the quantity of fatty acids present uncombined with glycerol. The acidity obtained by the official method (A. O. A. C. Book of Methods, p. 293, 1925) is calculated in terms of the percentage of oleic acid regardless of the acids actually present.

The value of this determination is dependent upon the fact that acidity develops in animal fats if they are allowed to be in contact with other animal tissues for any length of time after the animal is killed. Acidity also increases when fats are placed under unfavorable storage conditions, such as too high a temperature or an excess of moisture.

Since the producers of animal fats are not allowed to neutralize the acidity thus developed, the free fatty acid content of an animal fat gives some indication of the past treatment which the fat containing tissue has undergone. Producers of edible vegetable oils and fats are permitted to neutralize the fatty acids present in the crude oils, so that the refined products normally have a very low free fatty acid content. In the latter event, the free fatty acid content gives no indication of the past treatment of the fat.

A survey of the literature has indicated that fatty acids should be considered as possible catalysts in the process of rancidity development. Among the most important investigations along this line is one reported by Greenbank and Holm (1924). These workers found that free fatty acids catalyzed the autoxidation of butterfat, those of higher molecular weight exerting the greatest catalytic effect. Steam distillation of the butterfat, to remove these free acids, tended to greatly improve the keeping qualities of the butterfat.

It should be indicated at this point that the free fatty acid content of a fat does not necessarily denote the stage of rancidity development. Browne (1899) found that in the development of rancidity in butterfat, the first products formed were aldehyde substances and that these were then further oxidized to acids. Kerr and Sorber (1923) state that acids were not found in fats until the rancidity process was somewhat advanced, while Greenbank and Holm (1924) believe that the amount of moisture present in a fat determines whether an aldehyde or acid type of product is formed upon oxidation.

It should then be expected that the free fatty acid content of an animal fat might give some indication as to the keeping quality of the fat. That is, a high free fatty acid content would tend to indicate that the fat had received some mistreatment, either in the rendering process or in storage, and consequently was on the way to becoming rancid. Also, since the fatty acids catalyze the rancidity reaction, a fat having a high free fatty acid content might be expected to become rancid more rapidly.

The results of a study on two series of lard samples are given in Tables IV and V. Samples are arranged in the order of their increasing acidities. The keeping qualities of the shortenings are indicated by the length of their induction periods of oxygen absorption, since the latter was found to be more closely associated with keeping quality than any other single property. The length of induction periods in Table IV were obtained by the oxidation method with stirring at 95° C., and in Table V by the static oxidation method of Greenbank and Holm (1925) at 90° C. The results of each series, however, are comparable within themselves.

TABLE IV

COMPARISON OF THE FREE FATTY ACID CONTENT WITH THE KEEPING QUALITIES OF LARD SHORTENINGS AS DENOTED BY THE LENGTHS OF INDUCTION PERIODS OF OXYGEN ABSORPTION

Sample number	Free fatty acids as oleic	Length of induction period. Oxidation of 200 grams of shortening by the stirring method at 95° C.
	P.ct.	Hours
10	0.386	3.00
17	0.477	5.00
24	0.505	2.75
13	0.620	1.75
16	0.626	1.50
15	0.643	2.00
27	0.649	3.50
12	0.651	2.00
1	0.789	1.25
9	0.809	3.00
19	0.826	0.50
25	0.987	0.75
6	1.038	0.75

TABLE V

COMPARISON OF THE FREE FATTY ACID CONTENT WITH THE KEEPING QUALITIES OF LARD SHORTENINGS AS DENOTED BY THE LENGTHS OF INDUCTION PERIODS OF OXYGEN ABSORPTION

Sample number	Free fatty acids as oleic	Length of induction period. Oxidation of 20 grams of shortening by the static method at 90° C.
	P.ct.	Hours
5959	0.261	2.75
5967	0.340	6.25
5960	0.455	2.00
5961	0.478	3.75
5958	0.539	3.75
5962	0.761	1.25
5988	0.851	1.00

An examination of these data indicate that the shortenings exhibit no regular progression in decreased length of induction period with increasing acidity. However, it should be noted that those fats with outstandingly low free fatty acid values in each series also have the longer induction periods, while, conversely, those fats with outstandingly high acidities, have the short induction periods indicative of poor keeping qualities.

The results of this part of the study might be summarized as folows: The free acidity present in a fat is not distinctive of rancidity, but indicates, in a general way, what has happened to the fat during its processing and storage. An outstandingly low free fatty acid content usually indicates a good keeping fat, and the reverse is also true. On the basis of this, the free fatty acid determination is of significance but cannot by itself be used as an index of the keeping quality of a fat.

Iodine Number as a Criterion of the Keeping Ability of a Fat. The iodine number of a fat is defined as the number of grams of iodine absorbed by 100 grams of the fat under a specified set of conditions. It is thus a relative measure of the number of unsaturated bonds present in the fat. Since the first step postulated in the theory of rancidity development of fats is the addition of oxygen to the unsaturated glycerides, it might be assumed that a correlation should exist between the ease with which a fat becomes rancid and its iodine number. Such a relationship would no doubt exist if the unsaturated glycerides of fats were all of the same type. This is not true, however, for each kind of fat is composed of saturated glycerides with varying proportions of one or more of the unsaturated types, as oleic, linolic, or linolenic acid glycerides. Furthermore, the more highly unsaturated glycerides such as those derived from linolic and linolenic acids are likely to be selectively oxidized in preference to oleic acid glycerides.

It thus appears that the ease with which a fat absorbs oxygen, is not so much dependent upon the total amount of unsaturation as upon the variation in the kinds of unsaturated glycerides present. Accordingly, no general correlation might be expected between the iodine number of a shortening and its keeping ability. The results of studies to determine whether or not such a correlation existed are given in Tables VI and VII. The keeping quality of the shortening is indicated by the length of induction period determined by the stirring oxidation method as recorded in Table VI, and the static oxidation method as recorded in Table VII. The data indicate that there is no uniform relationship between the iodine number and the keeping qualities of a shortening. Restricting the comparison to one type of shortening, presumably containing the same unsaturated glycerides, it appears that there is a slight tendency for those samples having the lower iodine numbers to have the better keeping qualities.

Smoking Temperature versus Keeping Quality. Blunt and Feeney (1915) devised a method whereby they determined the temperature at which the sample began to smoke when heated up gradually in an evaporating dish over a free flame. This smoking temperature would vary with the proportion of saturated to unsaturated glycerides in the fat and with the type of unsaturated glycerides found. They also found that it could be lowered by increasing the acidity. These considerations would tend to point toward the possibility of a relationship between the decomposition or smoking temperature of a fat and its susceptibility to rancidity development.

The smoking temperatures of a series of shortenings as compared with their keeping quality, are listed in Table VIII. The keeping quality is designated by the length of induction period of oxygen

TABLE VI

COMPARISON OF THE IODINE NUMBERS WITH THE KEEPING QUALITIES OF SHORTENINGS AS DENOTED BY THE LENGTH OF INDUCTION PERIODS

Sample number	Type of shortening	Iodine number (Hanus method)	Length of induction period in hours. Oxidation of 200 grams of shortening by the stirring method at 95° C.
15	Prime steam lard	57.1	2.25
28	Open kettle lard	58.3	3.50
24	Open kettle lard	59.4	2.25
12	Prime steam lard	61.7	2.00
4	Prime steam lard	62.0	0.75
25	Prime steam lard	62.5	4.50
17	Open kettle lard	63.8	5.00
9	Prime steam lard	63.9	3.00
19	Prime steam lard	63.9	0.50
16	Prime steam lard	64.1	1.50
27	Prime steam lard	64.2	3.50
1	Open kettle lard	65.5	1.25
6	Prime steam lard	65.5	0.75
10	Open kettle lard	65.7	3.00
13	Open kettle lard	82.7	1.75
5	Oleo oil	45.4	0.50
31	Oleo oil	45.9	0.75
36	Oleo oil	46.6	1.00
3	Oleo oil	48.8	1.75
21	Compound	88.1	0.50
30	Compound	91.3	0.50
26	All-hydrogenated	75.6	3.50
29	All-hydrogenated	76.5	3.25
7	All-hydrogenated	78.7	2.00
2	All-hydrogenated	78.8	2.75
8	All-hydrogenated	79.8	1.00
18	All-hydrogenated	83.2	4.75

TABLE VII

COMPARISON OF THE IODINE NUMBERS WITH THE KEEPING QUALITIES OF SHORTENINGS AS DENOTED BY THE LENGTH OF INDUCTION PERIOD

Sample number	Type of shortening	Iodine number (Hanus method)	Length of induction period in hours. Oxidation of 20 grams of shortening by the static method at 90° C.
5967	Open kettle lard	57.2	5.75
5959	Prime steam lard	58.9	2.75
5988	Open kettle lard	65.0	1.00
5961	Prime steam lard	65.8	3.25
5958	Prime steam lard	66.3	3.25
5962	Open kettle lard	66.4	1.25
5960	Prime steam lard	66.7	2.00
5990	Oleo oil	47.8	3.50
5954	All-hydrogenated	62.4	——
5956	All-hydrogenated	62.5	39.50
5955	All-hydrogenated	66.5	23.00
5957	All-hydrogenated	67.4	32.50

TABLE VIII

COMPARISON OF SMOKING TEMPERATURES WITH THE KEEPING QUALITIES OF SHORTENINGS AS DENOTED BY THE LENGTH OF INDUCTION PERIOD

Sample number	Type of shortening	Smoking temperature	Length of induction period. Oxidation of 20 grams of shortening by the static method at 90° C.
		°C.	Hours
5988	Open kettle lard	153	1.00
5962	Open kettle lard	156	1.25
5958	Prime steam lard	159	3.25
5960	Prime steam lard	160	2.00
5959	Prime steam lard	167	2.75
5961	Prime steam lard	169	3.25
5967	Open kettle lard	182	5.75
5990	Oleo oil	161	3.50
5956	All-hydrogenated	214	39.50
5954	All-hydrogenated	216	——
5957	All-hydrogenated	217	32.50
5955	All-hydrogenated	224	23.00

absorption when the fats were oxidized at 90° C. by the static method.

The hydrogenated fats were found to have the highest smoking temperatures and as a group possessed the best keeping qualities. The oleo oil and lard samples had somewhat similar decomposition temperatures and also possessed keeping qualities of the same order, as evidenced by the length of induction periods.

The smoking temperatures were found to have about the same relationship to keeping qualities of the lard samples as were found for the iodine numbers and free fatty acid contents. That is, these

TABLE IX

"COEFFICIENTS OF RANK OF CORRELATION" BETWEEN THE KEEPING QUALITY OF SHORTENINGS, DENOTED BY THE LENGTH OF THEIR INDUCTION PERIODS, AND THE FREE FATTY ACID CONTENTS, IODINE NUMBERS, AND SMOKING TEMPERATURES

Factor	Correlation with the length of induction period of shortening in hours (keeping quality)
Table IV, Free fatty acids as oleic	$-.698 \pm .100$
Table V, Free fatty acids as oleic	$-.607 \pm .168$
Table VI, Iodine numbers (all shortenings)	$+.009 \pm .135$
Table VI, Iodine numbers (lards)	$-.348 \pm .160$
Table VI, Iodine numbers (all-hydrogenated)	$-.086 \pm .286$
Table VII, Iodine numbers (all shortenings)	$-.139 \pm .164$
Table VII, Iodine numbers (lards)	$-.428 \pm .217$
Table VIII, Smoking temperatures (all shortenings)	$+.861 \pm .052$
Table VIII, Smoking temperatures (lards)	$+.786 \pm .011$

samples having the highest decomposition point had the low iodine and fatty acid values and possessed the better keeping qualities. The samples having the lowest decomposition points possessed the higher iodine and fatty acid values and exhibited the poorest keeping qualities. The limited data accumulated are scarcely adequate to a general conclusion, but smoking temperature appeared to be more definitely correlated with autoxidation induction period than did the iodine number.

The coefficients of rank of correlation noted in Table IX obtained by the formula of Jackson (1924) reemphasize the fact that the smoking temperature of shortenings is a fair index of their keeping quality, that the free fatty acid content is also significant, but that the iodine numbers are of little significance in this respect.

Effect of Storing Crackers in an Atmosphere of CO_2 and in Various Humidities Upon Their Keeping Quality

Ritsert (1890) found that lard stored in an atmosphere of hydrogen or nitrogen did not become rancid, but when stored in CO_2 the lard absorbed some of the gas and acquired a tallowy taste. Later workers, Emery and Henley (1922), and Holm, Wright, and Greenbank (1927) also found that an atmosphere of CO_2 did not behave as an inert gas and prevent the development of rancidity. On the basis of the work of these investigators, there seemed to be little reason to suspect that CO_2 would prevent the development of rancidity in crackers, although there still remained the possibility that rancidity development might be delayed to an appreciable extent. Cracker samples made with cottonseed oil as a shortening agent were stored at 40° C. in CO_2 and air. After two weeks, the cans were opened and examined. It was found that the samples stored in carbon dioxide were rancid as well as the control samples. Carbon dioxide appeared to have no substantial effect in delaying the onset of rancidity in crackers.

Moisture is considered as one of the prime requirements for the development of hydrolytic rancidity and as somewhat of a negative catalyst in oxidative rancidity development. Greenbank and Holm (1924) refer to the action of moisture in lengthening the induction period of oxygen absorption of fats while Fine and Olsen (1928) call attention to the preservative action of moisture in delaying the progress of rancidity or tallowiness in grain products.

A study was made of the development of rancidity in crackers when stored in various humidities. The cracker samples, ground to a meal with a mortar and pestle, were placed in large Petri dishes and stored in the desiccators over sulphuric acid solutions of various concentra-

tions. The atmosphere in contact with these solutions was thus maintained at various levels of aqueous vapor pressure.

Preliminary work indicated that the storage of crackers over concentrated sulphuric acid caused them to acquire rancid properties more quickly than controls stored under ordinary atmospheric conditions; that atmospheres of 10–30% relative humidity preserved crackers similar to the controls, while atmospheres of 50–75% relative humidity caused the crackers to become musty. The results obtained by a representative study made on one cracker sample are given in Table X.

TABLE X

EFFECT OF RELATIVE HUMIDITY ON THE AMOUNT OF MOISTURE IN CRACKERS AND THEIR KEEPING QUALITIES

Relative humidity (calculated)	Moisture in the crackers	Crackers after 32 days storage			Crackers after 59 days storage		
		Smell	Taste	Kreis test	Smell	Taste	Kreis test
P.ct.	P.ct.						
0[1]	0.84	Good	Good	Positive	Off	Off	Positive
1	1.67	Good	Good	Negative	Good	Good	Positive
5	2.87	Good	Good	Negative	Good	Good	Positive
30	5.78	Good	Good	Negative	Good	Good	Positive
Atmospheric humidity	5.48	Good	Good	Negative	Good	Good	Positive

[1] Over concentrated H_2SO_4. Some water vapor was probably present in the chamber.

It is evident from the table that 0% relative humidity favors the development of oxidative rancidity and that any humidity over 0% retards this development. Since commercial crackers contain at least 5–6% moisture there would appear to be little danger that oxidative rancidity would develop in them through too low a moisture content.

Effect of Reheating Crackers on Their Keeping Qualities

The influence of reheating and overbaking of crackers on the resulting keeping qualities of the crackers should be of interest to the practical baker. Especially is it of interest in determining how the reheating or "crisping" of crackers as practiced by the restaurants affects the keeping quality of the crackers.

The results of a study on the effect of reheating a cracker sample, made with lard as a shortening agent, on its keeping qualities are expressed graphically in Figure 1. It is evident that reheating the crackers twice for five minute intervals at 400° F. was sufficient to cause a deterioration in their keeping qualities as was shown by the increased rate of oxygen absorption when they were oxidized. Reheating four and six times at 400° F., for five minute intervals, caused

a marked deterioration in the cracker samples. This study points out the necessity of avoiding repeated reheating of crackers in this manner.

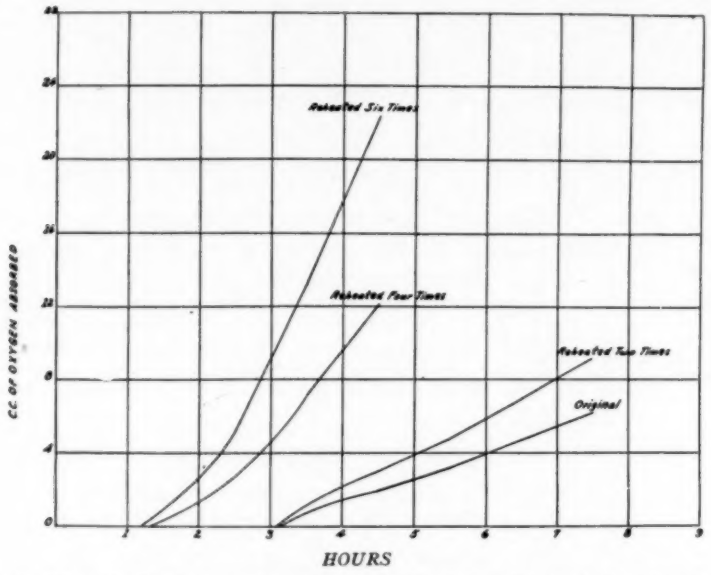

Fig. 1. Effect of reheating a cracker sample on its keeping qualities as indicated by its oxygen absorption, when 100-gram samples were oxidized by the static method at 90° C. Sample reheated two, four, and six times for five minute intervals at 400° F.

Effect of Temperature of Baking on Keeping Quality

The fact that reheating cracker samples caused them to increase greatly in their rate of oxygen absorption when oxidized, raised the question of the effect of the baking temperature and the length of time of baking of crackers on their keeping qualities. Data in regard to the conditions of baking of crackers were secured from each commercial bakery along with the shortening and cracker samples. These data are presented in Table XI.

There appears to be no relationship between the keeping quality of crackers and variations in baking temperature and length of time of baking. The moisture content of the crackers during the baking process is evidently high enough to prevent the crackers from being excessively heated even though the oven temperature is very high or the length of baking long.

Hydrogen-ion Concentration of Crackers in Relation to Their Keeping Quality

The fact that acids act as catalysts in the development of oxidative rancidity, raised the question of the possible significance of hydrogen-

TABLE XI

EFFECT OF THE CONDITIONS OF BAKING ON THE KEEPING QUALITY OF CRACKERS

Sample number	Type of shortening used in the crackers	Days until crackers developed rancid odor on storage at 40° C.	Conditions of baking of the crackers. Temperatures in degrees Fahrenheit
5954	All-hydrogenated	[1]	435° for 3.75 minutes
5956	All-hydrogenated	[1]	500° for 4.25 minutes
5955	All-hydrogenated	166	525° for 4.00 minutes
5957	All-hydrogenated	125	515° for 3.75 minutes
26	All-hydrogenated	87	——
29	All-hydrogenated	87	——
2	All-hydrogenated	87	550° .....
7	All-hydrogenated	77	540° .....
18	All-hydrogenated	49	475° for 4.50 minutes
8	All-hydrogenated	41	450° for 5.00 minutes
5990	Oleo oil	[1]	525° for 5.00 minutes
21	Compound	41	——
30	Compound	28	550° .....
17	Open kettle lard	72	475° for 4.50 minutes
5967	Open kettle lard	69	495° for 4.25 minutes
5988	Open kettle lard	68	475° for 5–6 minutes
25	Prime steam lard	49	590° for 5.50 minutes
9	Prime steam lard	49	450° for 5.00 minutes
5958	Prime steam lard	48	485° for 4.00 minutes
5962	Open kettle lard	48	420° for 4.25 minutes
4	Prime steam lard	45	515° .....
10	Open kettle lard	41	450° for 5.00 minutes
24	Open kettle lard	41	575° for 4.50 minutes
5961	Prime steam lard	41	450° for 6.00 minutes
15	Prime steam lard	37	600° .....
13	Open kettle lard	37	535° for 3.00 minutes
5959	Prime steam lard	36	..... 4.00 minutes
6	Prime steam lard	28	485° for 3.50 minutes
27	Prime steam lard	23	500° for 5.00 minutes
16	Prime steam lard	23	515° for 4.00 minutes
28	Open kettle lard	18	500° for 5.00 minutes
1	Open kettle lard	18	490° .....
19	Prime steam lard	18	——
5960	Prime steam lard	3	510° for 3.00 minutes

[1] Sweet at the end of 195 days storage.

ion concentration to the keeping qualities of crackers. Bailey and Johnson (1924) determined the hydrogen-ion concentration and keeping quality of 60 samples of commercial crackers. Of these samples, 75% gave extracts on the alkaline side of neutrality and the remaining 25 % were on the acid side. They found that the percentage of alkaline crackers which became rancid was about the same as for the acid crackers, and the conclusion necessarily followed, that there was no correlation between the reaction of crackers and their keeping qualities.

The conclusion of Bailey and Johnson was substantiated by similar studies on two series of commercial crackers, the results of which are given in Table XII. Hydrogen-ion concentration was determined

TABLE XII

HYDROGEN-ION CONCENTRATION OF CRACKERS IN RELATION TO THEIR KEEPING QUALITIES

Sample number	Type of shortening used	pH of crackers	Days until crackers developed a rancid odor on storage at 40° C.
12	Prime steam lard	8.83	28
25	Prime steam lard	8.67	49
15	Prime steam lard	8.61	37
10	Open kettle lard	8.46	41
17	Open kettle lard	8.44	72
9	Prime steam lard	8.15	49
27	Prime steam lard	8.03	23
5959	Prime steam lard	8.01	36
1	Open kettle lard	7.94	18
28	Open kettle lard	7.93	18
5961	Prime steam lard	7.79	41
19	Prime steam lard	7.67	18
5958	Prime steam lard	7.63	48
16	Prime steam lard	7.60	23
6	Prime steam lard	7.60	28
5962	Open kettle lard	7.57	48
5988	Open kettle lard	7.51	58
5967	Open kettle lard	7.47	68
13	Open kettle lard	7.28	37
24	Open kettle lard	7.04	41
4	Prime steam lard	6.45	45
18	All-hydrogenated	8.62	49
29	All-hydrogenated	8.44	87
7	All-hydrogenated	8.15	77
8	All-hydrogenated	8.09	41
2	All-hydrogenated	7.95	87
5957	All-hydrogenated	7.61	125
5955	All-hydrogenated	7.53	166
5956	All-hydrogenated	7.45	Sweet at end of 195 days
5954	All-hydrogenated	6.66	Sweet at end of 195 days
26	All-hydrogenated	6.52	87
21	Compound	8.73	41
30	Compound	7.40	28
5990	Oleo oil	6.33	Sweet at end of 195 days
22	Corn oil	8.44	45

electrometrically on cracker extracts using a Type K potentiometer and a Bailey electrode. The keeping quality of crackers was determined by storing the crackers at 40° C., and noting the length of time until they developed a rancid odor.

Bailey and Johnson found 25% of the cracker samples studied had an acid reaction. In Table XI only 4 cracker samples out of 35, or 11%, had an acid reaction, but in no case did any of the acid crackers

have inferior keeping qualities and no correlation was evidenced between the reaction of crackers and their keeping quality.

Summary and Conclusions

1. Shortenings stored unexposed to air retained their keeping qualities much better than those open to the air. A refrigerator temperature (10° C.) decreased the tendency of the shortenings to become rancid but was not nearly so effective as the exclusion of air.

2. Iodine numbers of shortenings do not appear to be related to keeping qualities. Free fatty acid content, and to a greater extent the smoking temperatures of shortenings are distinctly correlated with keeping qualities. Coefficients of rank of correlation are given for these factors.

3. Crackers stored in carbon dioxide gas became rancid as quickly as when stored in air.

4. Oxidative deterioration of crackers was found to be favored by an atmosphere of 0% relative humidity, while humidities of 1% or greater appeared to be protective.

5. Reheating crackers for 5-minute intervals at 400° F., for crisping was found to markedly accelerate their oxidative deterioration. Temperature and length of baking of commercial crackers exerted no influence on the keeping quality since the moisture content of the crackers was evidently high enough during the baking process to prevent the crackers from being excessively heated, even though the oven temperature was high or the length of baking long.

6. No relationship was found between the keeping quality of commercial crackers and their H-ion concentration.

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ON THE VITAMIN B CONTENT OF BREAD

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It has been proven that the low nutritive value of polished rice, the staple food of the Japanese, particularly its lack of vitamins is the cause of beriberi and other diseases. Due, in part, to this phenomena, the use of wheat bread has been gradually increasing in Japan.

The extent to which vitamin B occurs in bread is controversial. It is maintained by some, that bread contains sufficient vitamin B, while others state that even though there was sufficient vitamin B present in bakers' yeast and the other raw materials used in bread making, the vitamin would be entirely destroyed at the high temperatures to which bread is subjected during baking. It is our aim to contribute some investigational data to help answer this very interesting question.

Many investigations have been undertaken both in Japan and abroad on the question of the occurrence of vitamin B in bread. We will not endeavor to completely survey the literature, merely mentioning some outstanding contributions on this subject. Bernfeld and Schliff [1] made comparative tests with bread which had been raised with baking powder and with bakers' yeast. Mice were fed with these two kinds of bread. The results conclusively proved the inferiority of the bread which had been raised with baking powder. Scheunert and Schieblich [2] have published the results of several of their researches in relation to the vitamin content of bread. According to their experiments, pigeons or mice can be raised normally on bread which has been leavened with a large amount of bakers' yeast. However, they found that it required from 5 to 6 times more bakers' yeast than is usually used, to produce normal growth. They pointed out that the bread made with this quantity of bakers' yeast was much different in appearance than ordinary bread. Scheunert and Schieblich also reported, that vitamin B of brewers' yeast had about the same growth promotive effect as bakers' yeast, but pointed out, that brewers' yeast had 2 to 3 times more antineuritic properties than bakers' yeast.

[1] Bernfeld, A. and Schliff, E., Biochem. Zeit., 1930, **224**: 434.
[2] Scheunert, A. and Schieblich, M., Biochem. Zeit., 1928, **202**: 380; ibid., **212**: 80.

The Japanese investigators, Tadera [3] and Yokomaki,[4] working in the laboratories of Dr. Shimazono of the Tokyo Imperial University, conducted a number of investigations with respect to the quantities of vitamin B in foodstuffs. According to their experiments, particularly with bread, pigeons fed exclusively on white bread were all taken ill and died within 16 to 36 days. However, when a small quantity of brewers' yeast was given to the pigeons daily, they gained in weight and remained in good health. Likewise, when the pigeons were fed with whole-wheat bread they remained in good health for over 3 months. From the results of their experiments, Tadera and Yokomaki concluded that the lack in nutritive qualities of white bread was mainly due to deficiencies in vitamin B content.

The Problem

The question, therefore, arises as to how much brewers' yeast should be added to bread, as ordinarily made, to provide for a sufficient amount of vitamin B. According to Veselkin, et al.,[5] feeding experiments with pigeons using white bread containing varying amounts of bakers' yeast, and additions of brewers' yeast (dried at 40° C.), showed that 0.2 grams of dried brewers' yeast fed separately, daily; with white bread fed freely, provided sufficient vitamin B to maintain weight and prevent polyneuritis. Veselkin and his coworkers further stated, that inasmuch as 0.5% of brewers' yeast was needed in their experiments to provide sufficient vitamin B with a vitamin-B-free basal diet, that white bread containing 0.5% of bakers' yeast provided only one-half of the vitamin necessary to maintain weight. Attempts to increase the vitamin content of white bread, by using bakers' yeast in amount equal to 6% of the total weight of the bread, were unsuccessful. However, the addition of dried brewers' yeast to the dough produced a bread on which pigeons maintained constant weight. From their investigations, Veselkin, et al., concluded that, by the addition of dried brewers' yeast as an ingredient in the manufacture of white bread, bread of adequate vitamin content could be prepared for human consumption and without a change in taste. Bennion [6] also stated that dried brewers' yeast is sold as a bread improver because of its vitamin B content.

Finally, the senior author of the paper (Hashitani [7]) in reporting on the results of several years of research on the physiology of yeast and the utilization of waste yeast, suggested the use of brewers' yeast in bread making.

[3] Tadera, M., Iji-Shimbun, 1929, 1249.
[4] Yokomaki, A., Iji-Kōron, 1930, 915.
[5] Veselkin, N. V., et al., Chem. Abst., 1929, 3253.
[6] Bennion, E. Bread making, its principles and practice. Oxford University Press, London.
[7] Hashitani, Y., Japanese Jour. Ryōshoku Kenkyu., 1930, 63.

Experimental

In order to determine the influence of dried brewers' yeast upon the nutritive properties of bread, the following experiments were undertaken:

Methods and Materials Used

Bread which had been baked from doughs into which various quantities of dried brewers' yeast had been added was fed to pigeons. By such a procedure it was possible to observe the nutritive defects of white bread; when such defects are eliminated by the use of brewers' yeast, and also what the minimum quantity of brewers' yeast is, which will overcome nutritive defects. The bread used in these tests was made in an experimental way in the laboratory of the Dai Nippon Brewery Company. The bread was always baked under identical conditions, lest there should be any differences in the bread itself. A straight dough method was used, the dough being mixed according to the following formula:

Wheat flour	1350 gms.
Cane sugar	45 "
Compressed yeast	22 "
Salt	15 "
Butter	30 "
Water	738 "

Definite quantities of brewers' yeast were added to the above at the time of mixing. Fermentation time was 135 minutes, (90 minutes to first punch, 45 minutes to second punch), proofing time 50 minutes. The loaves were baked at an oven temperature varying between 200° and 215° C. for 50 minutes. Duplicate loaves having the following dimensions were obtained: width, 10 cm.; length, 25 cm.; and depth, 15 cm. The composition of the bread used in the experiments, with special reference to the dried brewers' yeast content of the bread, is given in Table I. The dried brewers' yeast used in these tests is a product of the brewery with which the authors are associated. It is

TABLE I

COMPOSITION OF BREAD USED IN THE EXPERIMENTS

Sample number	Percentage of dried brewers' yeast in the dough	Percentage of dried brewers' yeast in the baked bread
A	1.0% addition	about 1.2%
B	0.5% addition	about 0.6%
C	0.4% addition	about 0.48%
D	0.3% addition	about 0.36%
E	Brewers' yeast-free	
F	White bread purchased at a local bakery	
G	White bread purchased at a local bakery	
H	Brown bread purchased at a local bakery	

made by a patented drying process which prevents deterioration of any of the active substances in the yeast itself.

Results of the Feeding Tests with Pigeons

For these tests the pigeons were divided into five groups and fed with only the particular bread under test and water. Every morning a definite quantity of food was left with the pigeons for them to take as they chose. Each pigeon ate from 20 to 60 grams of bread per day. Observations were made with respect to their movements, condition of feather, and appetite. They were weighed every other day.

In the group in which the pigeons were fed with bread of high vitamin content, the appetites of the pigeons increased and they ate more food. As a result their weight increased daily up to a certain point. On the other hand, those pigeons which were fed on vitamin-free bread lost their appetites, their weight likewise decreased daily. Details concerning each group of pigeons follow:

Group 1. The pigeons in this group were first fed with bread E (free of brewers' yeast) The pigeons gradually lost weight. Pigeon No. 1 of the group died on the 17th day. Pigeon No. 2 suffered from

Fig. 1. Showing pigeon No. 2 suffering from polyneuritis.

polyneuritis. A photograph of this pigeon while in this condition is shown in Figure 1. When the pigeon was fed with the dried brewers' yeast used in these tests, it soon recovered the health and vigor displayed in Figure 2.

Bread E (brewers' yeast-free) was replaced in the diet by bread B, (containing 0.5% of brewers' yeast). This bread was fed to pigeon

No. 3 which had previously lost considerable weight on bread made without the addition of brewers' yeast. Pigeon No. 3 rapidly regained its health and original weight. Then bread B was replaced by bread G

Fig. 2. Showing pigeon No. 2 after being fed with dried brewers' yeast.

(commercial white bread), the pigeons again suffered from polyneuritis owing to the absence of vitamin B. However, when subsequently fed with dried brewers' yeast this condition was completely overcome The pigeons in this group also recovered normal health when fed with

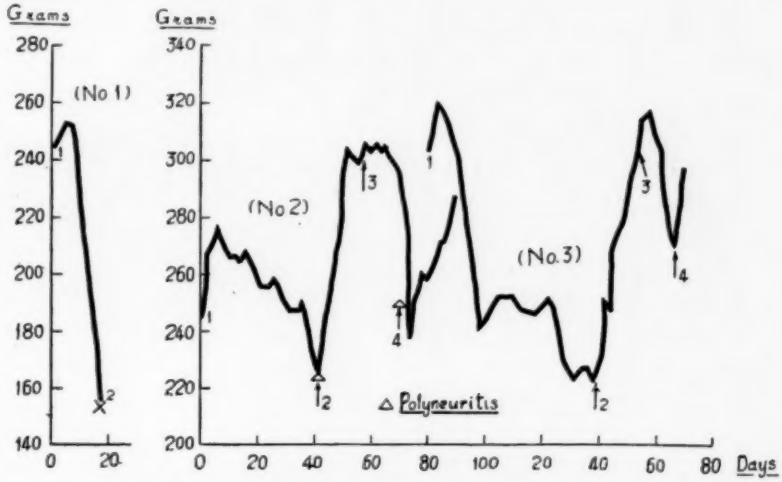

Fig. 3. 1–2 Bread which contained no brewers' yeast.
2–3 Bread which contained 0.5% brewers' yeast.
3–4 Bread sold in the market (G).
4 Bread which contained 0.4% brewers' yeast.

bread C (containing 0.4% of dried brewers' yeast). Figure 3 shows graphically the conditions of growth of the pigeons in this group.

Gorup 2. As was the procedure in the tests with the pigeons of *Group 1*, the first feeding was with the brewers' yeast-free bread (bread E). On this diet the pigeons lost considerable weight. The pigeons were then fed on bread D (containing 0.3% of dried brewers' yeast). In these tests, although the recovery was slower than in the tests where bread containing 0.5% of dried brewers' yeast was used, the pigeons gradually regained their normal weight and health. A growth chart for the pigeons studied in *Group 2* is shown graphically in Figure 4.

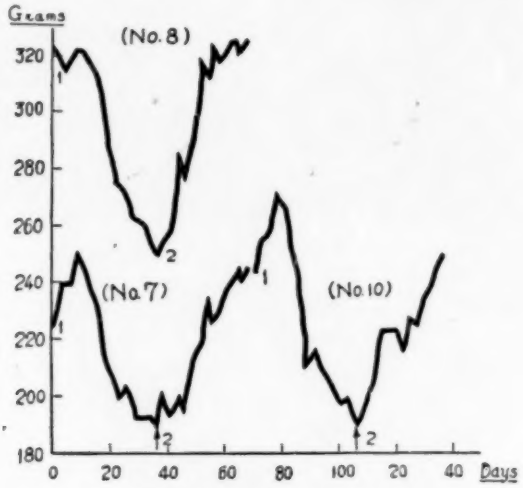

Fig. 4. 1–2 Bread which contained no brewers' yeast.
2 Bread which contained 0.3% brewers' yeast.

Group 3. The pigeons were first fed with bread F (commercially baked bread). The results were similar to those reported by other investigators. The pigeons grew extremely weak on the 18th day. Before the pigeons showed signs of polyneuritis they were fed with bread containing 0.5% of dried brewers' yeast. This bread proved very nourishing, so much so that at the end of 10 days the weight of the pigeons exceeded their weight at the start of the experiment. As the amount of dried brewers' yeast was successively lowered from 0.5% to 0.4%, and then to 0.3%, the pigeons showed no nutritional disturbances. Figure 5 shows the data graphically.

Group 4. The pigeons in this group were fed bread containing 0.5% of dried brewers' yeast from the start, in order to demonstrate its full nutritive value. This bread was then replaced by bread H, a supposedly whole wheat bread of commercial manufacture. Bread H

failed to maintain weight and acted similar to ordinary white bread. On close examination this bread (H) appeared to contain only a small

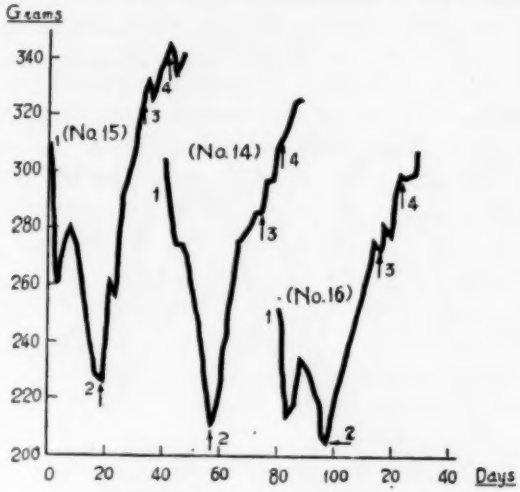

Fig. 5. 1–2 Bread sold in the market (F).
2–3 Bread which contained 0.5% brewers' yeast.
3–4 Bread which contained 0.4% brewers' yeast.
4 Bread which contained 0.3% brewers' yeast.

quantity of whole wheat, and was probably artificially colored. The growth chart for this series of tests is shown as Figure 6.

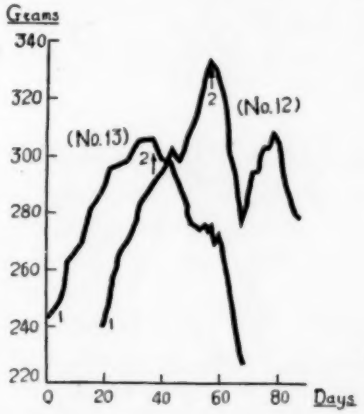

Fig. 6. 1–2 Bread which contained 0.5% brewers' yeast.
2 Brown bread sold in the market (H).

Group 5. The pigeons were first fed with bread containing 1% of dried brewers' yeast. Pigeons weight, as a matter of course increased gradually, reaching a certain peak. The bread containing 1% of dried brewers' yeast was then replaced with bread containing 0.3% of

this substance. The results were similar to those experienced in our tests with the pigeons studied in *Group 1* which had been fed brewers' yeast-free bread. One of the pigeons suffered from polyneuritis. Fed brewers' yeast separately the pigeon recovered from the disease. Two pigeons of this group were then fed with bread containing 0.5% dried

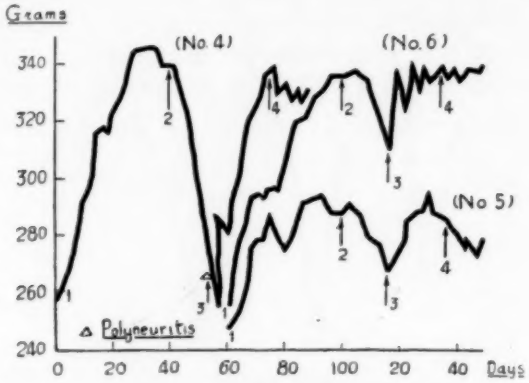

Fig. 7. 1–2 Bread which contained 1% brewers' yeast.
2–3 Bread which contained 0.3% brewers' yeast.
3–4 Bread which contained 0.5% brewers' yeast.
4 Bread which contained 0.3% brewers' yeast.

brewers' yeast instead of bread containing 0.3% of brewers' yeast and after the pigeons had regained their weight they were again fed bread containing 0.3% brewers' yeast. This time, however, the results were different from those experienced at the start of the tests with the pigeons of this group, namely, the pigeons gave evidence of only a slight

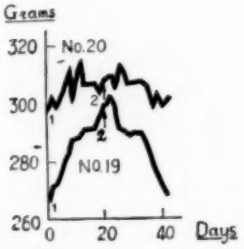

Fig. 8. 1–2 Bread which contained 1% brewers' yeast.
2 Bread which contained 0.3% brewers' yeast.

deficiency in vitamin B. It seemed strange to us that pigeons would suffer from polyneuritis when bread containing 1% of dried brewers' yeast was replaced with bread containing 0.3% of this substance; while they displayed evidences of only a slight deficiency in vitamin B when the dried brewers' yeast was gradually decreased from 1% to 0.5%, and then to 0.3%. However, the tests described with the

pigeons of *Group 5* were repeated and similar results were obtained. The growth charts for the tests carried out with the pigeons of *Group 5* are shown graphically in Figures 7 and 8.

Discussion

From the experiments just made it appears as if at least 0.3% of dried brewers' yeast was necessary in bread in order to preserve the health of pigeons. Bread containing 0.5% of dried brewers' yeast contained an excessive amount. It is to be concluded, therefore, that 0.4% of dried brewers' yeast is the proper amount. The addition of 0.3% of dried brewers' yeast was sufficient for pigeons of *Group 2*, while with *Group 5*, when bread containing 1% of brewers' yeast was replaced by bread containing 0.3% of dried brewers' yeast a great shortage in vitamin content was in evidence. This may have been due to the fact that the pigeons of *Group 5* had become accustomed to an excess of vitamin B when fed with bread containing 1% of brewers' yeast, and the sudden reduction in the amount of brewers' yeast to 0.3% made them feel the lack of vitamin B keenly. When, however, the amount of dried brewers' yeast was gradually reduced in the bread from 0.5% to 0.3%, no marked decline in the health of the pigeons was observed. Further, as a result of the experiments with the pigeons of *Group 3*, it was found that no unfavorable effects manifested themselves when the dried brewers' yeast in the bread was gradually reduced from 0.5% to 0.4%, and then to 0.3%. It is apparent, therefore, the white bread of commercial character can be improved, at least as measured by feeding experiments with pigeons, by the use of a small quantity of dried brewers' yeast (0.3% to 0.4%), in addition to the yeast used for leavening.

Effect of Heat and Hydrogen-ion Concentration on Vitamin B

According to Chick and Roscoe [8] vitamin B has the greatest resistance to heat at a hydrogen-ion concentration of pH 3 to 5. At this pH, there appears to be no loss in activity even when heated from 90°–100° C. for two hours.

To gather information on these points hydrogen-ion concentration values and temperatures developed during baking were determined. The data are shown in Tables II and III. From the data given in Table II it is apparent that the maximum temperature which developed during the baking of the loaf (temperature taken at the center of the loaf) was 98.5° C. This is no doubt due to the poor conductivity of the dough as well as to the evaporation of moisture from the dough. During the baking procedure the dough reaches temperatures of 90° C. and above for only 10 to 20 minutes.

[8] Chick, H. and Roscoe, M. H., J. Biochem. 1930, **24**: 105.

TABLE II

TEMPERATURE RELATIONS IN THE OVEN AND BREAD DURING BAKING

Time in minutes	0	5	10	15	20	25	30	35	40	45	50
Temperature ° C. inside of oven	150	181	200	202	204	206	211	210	211	215	215
Temperature ° C. in the center of bread	25	27	28	29.5	33	41	56.5	81	90	96.5	98.5
Temperature °C. near the crust of the bread	25	27.5	31	38	66	85	93	96	98.5	100	101

TABLE III

HYDROGEN-ION CONCENTRATION DEVELOPED DURING FERMENTATION AND IN THE BAKED BREAD

At the time of kneading	After first punch	After second punch	After proofing	Baked bread
pH 6.0	pH 5.8	pH 5.7	pH 5.6	pH 5.5

According to the data presented in Table III the pH of the dough at proofing time was 5.6. The pH of the finished loaf was 5.5. As pointed out in the paragraph above the temperature on the inside of the loaf reached 90°–100° C. for only a few minutes. It is to be concluded, therefore, that in the light of the investigations of Chick and Roscoe, and the data presented here, that vitamin B in bread is not decomposed by heat during the baking process. This point is further substantiated by the feeding experiments with pigeons discussed earlier. In these feeding tests, 50 grams of bread containing 3% of dried brewers' yeast maintained pigeons in good health. The amount of dried brewers' yeast in the 0.3% bread was approximately the same as that fed by Veselkin, et al., to pigeons independent of the bread taken during his tests.

In view of the results of the experiments just reported, it does not seem as though vitamin B is decomposed by heat when bread is baked. Likewise, this would be the case with such other raw materials containing vitamin B which are used in the baking of bread.

Summary

1. From the experiments made it is apparent that white bread is deficient in nutritive properties, particularly in vitamin B, such deficiences in nutritive properties may be compensated for by the use of other articles of food in the diet. The addition of small quantities of dried brewers' yeast has been found to be helpful in making good the nutritive defects of white bread. Furthermore, the addition of brewers' yeast does not affect the quality (palatability) of the bread.

2. The feeding tests made with pigeons with bread containing varying quantities of dried brewers' yeast indicate that the correct

amount of dried brewers' yeast which bread should contain to give perfect nutrition, at least for pigeons, is between 0.3% and 0.4%. These findings are in accord with those of Veselkin, et al., who supplied dried brewers' yeast alone with ordinary white bread.

3. From a study of the changes in hydrogen-ion concentration of the dough and the temperatures developed during the baking process, it was found that the pH of the dough at proofing time was 5.6, and that in spite of the high temperatures of the baking oven the temperature of the inner part of the loaf of bread did not quite reach 100 C. Furthermore, temperatures in excess of 90° C. were not exceeded for over 10 to 20 minutes.

4. The data mentioned in items 2 and 3 viewed in the light of the researches of Chick and Roscoe, with respect to the relationship between pH, temperature, and vitamin B activity, as well as in the similarity in the results of the feeding experiments of the authors with pigeons using bread in which the dried brewers' yeast had been incorporated as a baking ingredient, and the experiments of Veselkin, et als., who fed dried brewers' yeast along with ordinary white bread, seem to prove that vitamin B contained in bread is not decomposed by heat.

Finally, in making the observations that the nutritive value of white bread can be improved by the addition of dried brewers' yeast, it must be pointed out that there are not only marked differences in the quality of the fresh yeast used as raw material, but that the method of drying very seriously affects the quality of the dried yeast preparation. It is essential, therefore, that utmost care be made in the selection of yeast preparations and the manner in which they are handled.

A NOTE ON THE USE OF SELENIUM OXYCHLORIDE AS A CATALYST IN THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD

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Introduction

The past few years have seen a great improvement in the accuracy of the determinations carried out in the cereal laboratory. As collaborative results indicate, most routine analyses are now carried out with sufficient accuracy to warrant satisfaction.

Time is always an important factor in commercial laboratories. Particularly in mill control work, speed in getting the analysis reports back to the miller is essential. Therefore, besides striving for greater accuracy, control chemists are also continually endeavoring to shorten analytical methods in order to provide the greatest service for the production department.

Often times, a shorter protein determination would be of value to the grain department or to those in charge of making up the mill-mix.

The protein determination has been considerably shortened since Kjeldahl originated the method. As discovered by Kjeldahl the method consisted of merely digesting the sample with concentrated sulphuric acid alone, with the subsequent determination of the ammonia formed. This method of digestion required seven or eight hours.

Later, Wilfarth suggested the use of mercury as a catalyst. This modification shortened the digestion period.

Gunning's contribution to the method was the addition of anhydrous sodium or potassium sulphate to the digestion mixture. He also suggested the use of copper as a new catalyst. The use of copper required a hotter digestion temperature; this likewise shortened the time of digestion.

Copper is now a popular catalyst, and its use with a hot flame has further reduced the digestion time to about 60 minutes, or possibly a little less if the heaters are hot at the start. Copper has the advantage of being more convenient to use. A piece of copper wire dropped into the flask at the time of weighing the sample completes the task—no additional solutions are necessary. Furthermore, the formation of a

deep blue color and precipitate makes certain that an excess of sodium hydroxide has been added to make the solution alkaline in readiness for distillation.

There recently appeared a short paper by Lauro [1] on the use of selenium as a catalyst. The published data indicated that digestion time can be still further reduced. Experiments to verify the statements made in this paper were recently carried out in this laboratory.

Experimental

With the routine method, using a 2 gm. sample, 10 gms. of sodium sulphate, 0.15 to 0.20 gms. of copper wire, 25 cc. of H_2SO_4, and 550-watt electric heaters, the digestion time required is about 60 minutes; 50 minutes if the heaters are hot from the previous digestion. After digestion is complete the flasks are cooled about 15 minutes, making a total time of about 75 minutes. Distillation requires about 45 minutes. The total time consumed, assuming that the samples are weighed into the flasks during the distillation of the previous set, is over two hours. Aside from the time required, another objection lies in the fact that the still remains idle while the next set is cooling.

Selenium oxychloride, the compound used in these experiments, is a fuming liquid, and can be dispensed by means of a medicine dropper cut off to deliver a drop of the right size.

Preliminary tests indicated that 0.2 cc. of selenium oxychloride was sufficient if used in combination with a small piece of copper wire (about 0.05 gm.). The reason for adopting both catalysts was two-fold; the combination accelerates the reaction more than either one alone, and the indicator properties of copper, when sodium hydroxide is added, is useful.

It was found that when this combination of catalysts was used, that the samples during digestion cleared in less than 15 minutes, instead of in about 35 minutes when copper alone is used. Furthermore, digestion is complete in 30 minutes, starting with a cold heater. If the heaters are hot from the previous digestion the time is further reduced. Efforts to still further reduce the time were not made, because the time consumed during distillation was 45 minutes. Allowing 30 minutes digestion and 15 minutes cooling, the samples are ready for the still as soon as the previous set has digested. With the routine method, several minutes elapse before the next set is sufficiently cool to be diluted. By the use of selenium both the digestors and the still can be kept operating continuously. What is more important, however, is that the analysis of the samples is completed in 75 minutes instead of

[1] Lauro, M. F. Use of selenium as a catalyst in the determination of nitrogen by the Kjeldahl method. Ind. Eng. Chem. Analytical Edition, 3: 401, 1931.

110 minutes, the time the regular method utilizes, a saving in time of 35 minutes.

TABLE I

PROTEIN CONTENT OF WHEAT AND FLOUR AS DETERMINED BY THE USE OF COPPER ALONE AND IN COMBINATION WITH SELENIUM OXYCHLORIDE

Protein content of wheat				Protein content of flour			
Sample number	Copper alone	Copper plus selenium	Difference	Sample number	Copper alone	Copper plus selenium	Difference
	P.ct.	P.ct.	P.ct.		P.ct.	P.ct.	P.ct.
1	14.73	14.64	0.09	1	13.94	13.88	0.06
2	13.44	13.40	0.04	2	12.64	12.64	0.00
3	13.48	13.40	0.08	3	13.12	13.12	0.00
4	14.32	14.28	0.04	4	16.35	16.28	0.07
5	14.72	14.72	0.00	5	9.72	9.68	0.04
6	14.96	14.96	0.00	6	15.04	14.96	0.08
7	14.92	14.92	0.00	7	16.11	16.12	0.01
8	13.60	13.57	0.03	8	12.68	12.69	0.01
9	14.69	14.68	0.01	9	15.52	15.48	0.04
10	14.44	14.48	0.04	10	14.00	13.92	0.08
11	13.62	13.66	0.04	11	14.12	14.16	0.04
12	14.45	14.40	0.05	12	16.33	16.27	0.06
13	14.88	14.92	0.04	13	15.00	14.96	0.04
14	11.20	11.18	0.02	14	11.68	11.65	0.03
15	13.42	13.40	0.02	15	12.00	11.96	0.04

In Table I the results obtained from the analysis of 15 flour and 15 wheat samples are shown. All the figures given are the average of two or more determinations. Differences in results, considering both catalysts, are not any greater than the differences between duplicate determinations.

Unfortunately, our supply of selenium oxychloride became exhausted so that a more complete series of tests could not be made. However, the results obtained to date are sufficient to indicate the possibilities of the use of copper plus selenium oxychloride as catalytic agents in nitrogen determinations.

Conclusions

Preliminary experiments, using selenium oxychloride as a catalyst in combination with copper, indicate that a considerable saving in the length of time required for the determination of total protein content, can be expected from their use.

The cost of selenium oxychloride may exclude it from ordinary routine analyses, but during rush periods, when results are required in the shortest length of time possible, the addition of 0.2 cc. of selenium oxychloride to the digestion mixture will enable the operator to give more rapid service inasmuch as he will be able to report analyses at least half an hour sooner than by the method in which copper and sodium sulphate are used as the catalysts.

SOME RELATIONSHIPS INVOLVING CRUMB TEXTURE AND COLOR

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(Read at the Convention, May, 1931)

A single figure index of the quality of an experimental loaf of bread may convey a fully satisfactory summary of individual scores to any one worker who has become accustomed to evaluating separate criteria in a strictly proportional manner. If all workers were inclined to accept the same proportional weightings of individual scores, single figure indexes would undoubtedly be more generally used. That they are not is adequate evidence that individual judgments of the relative importance of the various crumb, crust, and dimensional evaluations of experimental loaves of bread are diversified. Moreover, the fact that particular characteristics of flours disappear entirely in single figure estimates of baking quality places that estimate at a disadvantage beside an itemized score. Crust, and more particularly crumb characters, are likely to be considered independently from measures of volume in describing test loaves for these reasons. It is, however, unfortunate that loaf volume alone is still used frequently as a sole measure of baking quality of a flour. Color, texture, and flavor of the crumb undoubtedly play major roles in determining the saleable value of a loaf of bread. Precision methods of scoring these variables would contribute greatly to a better evaluation of experimental baking tests. Tangible progress toward this end is manifest in the categorical scores already adopted by the American Association of Cereal Chemists, (Blish 1928, 1929).

Little appears to be known of the relationships between the chemical composition of flours and the crumb characters in different loaves produced under a standardized baking technique, or of relationships between those crumb characters and loaf volume. If the latter dimensional measure be accepted as the single criterion of flour quality, either the tacit assumption is made that crumb characters are very highly, if not perfectly correlated with loaf volume, or crumb characters are ignored or considered as being of little consequence in rating the flours.

In an endeavor to throw some light on these above relationships, a study has been made of the milling and baking records of the Minnesota State Testing Mill for the crop seasons of 1921 to 1926, inclusive. The data of these years have been presented fully by Bailey (1923, 1924), Bailey and Sherwood (1924) and Sherwood (1925, 1926, 1928). They are of unique value in the present connection in that the flours were of a uniform unbleached straight grade of commercial production in every case. Crumb characters of the loaves from the baking tests were judged in daylight, scores being awarded for color and texture by comparison with a single standard, as is the customary procedure in such work. Thus memory played a distinct role in the scoring of the crumb characters.

Results

It is clear from the coefficients of correlation between crumb characters and loaf volume presented in Table I that while both texture and color of crumb are positively related to loaf volume, the correlation is of a very small order. Texture shows the more consistent relationship with volume, and the higher average correlation. Crumb color, in one year, 1923, showed a negative correlation with loaf volume, but on the whole in the other years received a higher score as volume increased. It is obvious from these low correlations that the acceptance of loaf volume as the sole index of baking quality of flours from hard red spring wheats infers that the color and texture of the crumb are of practically no importance in determining quality of bread.

TABLE I

CORRELATIONS BETWEEN CRUMB CHARACTERS AND LOAF VOLUME

Crop season	N	Texture and loaf volume	Color and loaf volume
1921	52	+.096±.093	+.007±.094
1922	59	+.229±.083	+.224±.083
1923	60	+.066±.087	−.133±.086
1924	55	+.210±.087	+.265±.085
1925	57	+.218±.085	+.189±.086
1926	49	+.329±.086	+.254±.090
Weighted average	332	+.188±.036	+.131±.036

Like loaf volume, crumb texture may well be related to the quantity of protein in the flour. If that be so, then possibly the correlation between texture and volume shown in Table I may be due to the common relationship of both to the protein percentage in the flour. To test these possibilities the correlations between protein and texture for the six crop seasons have been computed, together with the partial correlations between loaf volume and crumb texture for constant

protein in the flour. The coefficients are presented in Table II, together with the analogous relationships involving crumb color.

TABLE II

CORRELATION COEFFICIENTS WITH PROTEIN IN FLOUR AND WITH LOAF VOLUME FOR CONSTANT PROTEIN, OF CRUMB TEXTURE AND COLOR

Crop season	N	Texture and protein in flour	Texture and loaf volume for constant protein in flour	Color and protein in flour	Color and loaf volume for constant protein in flour
1921	52	$-.01\pm.09$	$+.11\pm.09$	$+.14\pm.09$	$-.05\pm.09$
1922	59	$+.22\pm.08$	$+.16\pm.09$	$+.22\pm.08$	$+.15\pm.09$
1923	60	$+.30\pm.08$	$-.02\pm.09$	$-.22\pm.08$	$-.07\pm.09$
1924	55	$+.26\pm.08$	$+.10\pm.09$	$+.05\pm.09$	$+.28\pm.08$
1925	57	$+.37\pm.08$	$+.04\pm.09$	$+.17\pm.09$	$+.12\pm.09$
1926	49	$+.51\pm.07$	$-.05\pm.10$	$+.50\pm.07$	$-.19\pm.09$
Weighted average	332	$+.27\pm.03$	$+.06\pm.04$	$+.13\pm.04$	$+.04\pm.04$

The average coefficient of $+ .27 \pm .03$ between protein and texture appears to represent fairly the general tendency of association in any crop season between these two variables. Any one of the discrepancies between the individual seasonal correlations and the average correlation is attributable simply to random sampling. Thus the texture of the crumb tends to improve as protein in the flour increases. The partial correlations between texture and volume for constant protein show clearly that crumb texture is not related to loaf volume except insofar as both are related to the protein content of the flour. Crumb color tends to a lesser degree to show the same associations.

Crumb color and crumb texture are significantly related to one another in the data considered herein. This is apparent from the coefficients of correlation given in Table III. That this is not due to the relationship of both these characters with the amount of protein present in the flour is shown by the partial correlations where protein is held constant. There can be little question but that the texture of the bread must influence one's judgment of its color, since texture very directly influences the extent of the shadows in the crumb and the nature of the light dispersal at the surface. It is possible that the correlations in Table III include a relatively large positive increment on account of this difficulty of making fine distinctions with regard to color when the amount and nature of the shadows varies with the texture of the crumb.

It is of interest to note the changes in average values of the two crumb scores for the different crop seasons. The average score for crumb color has varied from season to season (Table IV) over a range

TABLE III

GROSS CORRELATIONS BETWEEN COLOR AND TEXTURE OF CRUMB, AND THE PARTIAL CORRELATIONS WHEN PROTEIN IN THE FLOUR IS HELD CONSTANT

Crop season	N	Gross correlations	Partial correlations
1921	52	+.369±.081	+.358±.082
1922	59	+.156±.086	+.113±.087
1923	56	+.325±.081	+.414±.075
1924	54	+.529±.066	+.537±.065
1925	54	+.598±.059	+.563±.063
1926	49	+.755±.041	+.670±.053
Weighted average	324	+.446±.030	+.434±.030

of 1.2 units, and in a manner as might be anticipated, that is, without any orderliness between seasons. Such is not the case, however, for the average crumb texture. For the first five years the average texture score decreased steadily from 99.1 to 96.8, rising in 1926 to 98.4. This progressive change suggests at once an increasing severity of the operator's judgment in scoring texture. With only one standard of comparison, and that at the top of the scale, for such a tendency to manifest itself seems entirely logical. It must be borne in mind, however, that plausibility does not constitute proof. This feature of the data presented merely indicates the advisability of not attempting to set up such a scale based on human judgment when only one point on it is checked from time to time against a standard.

TABLE IV

AVERAGE SCORES FOR CRUMB COLOR AND CRUMB TEXTURE FOR SIX CROP SEASONS

Crop season	N	Crumb color	Crumb texture
1921	52	97.9	99.1
1922	59	97.2	98.8
1923	56	97.6	97.9
1924	54	97.5	97.1
1925	54	96.9	96.8
1926	49	98.1	98.4

While the correlations of percentage ash in the wheat and percentage ash in the flour with texture are not as yet available for this series of data, it is interesting to note here, without presenting the coefficients, that the percentage ash shows no relationship with color. Nor does the diastatic activity measured in 1925 and 1926 show any correlation with either of the two crumb characters. The moisture content of the grain also fails to show any relationship with the color or texture of the loaf of bread.

Perhaps the most interesting of the correlations involving crumb characters presented above is that between percentage protein in the

flour and texture of the bread made therefrom. These coefficients, given in Table II, show an average correlation of + .27 ± .03 between the two variables. The full scatter diagrams of the relationship in each season have been prepared and are reproduced in Figure 1. The

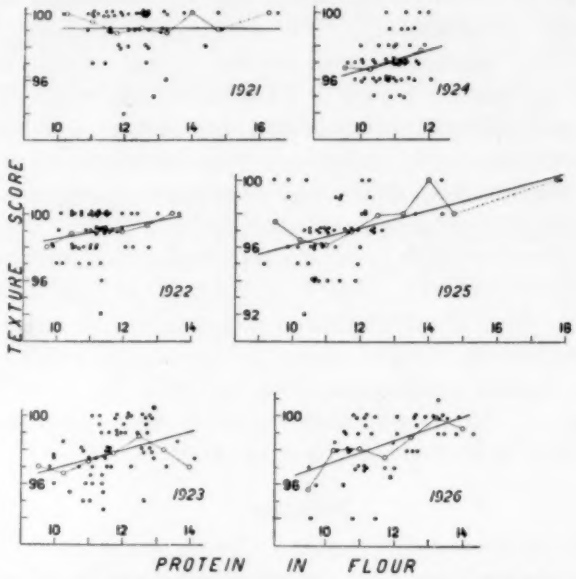

Fig. 1. Scatter diagram with theoretical and empirical regression lines for the relationship of texture score of the crumb to percentage protein of the flour in six individual crop seasons of hard red spring wheat.

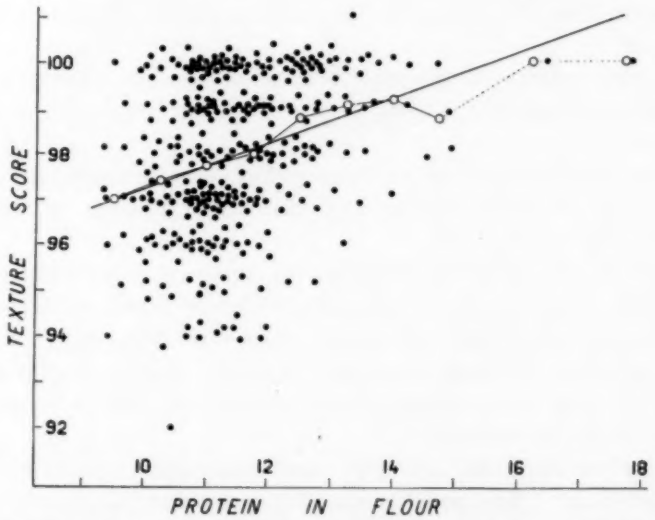

Fig. 2. A grouping of the six individual scatter diagrams (1921 to 1926 crop seasons) given in Figure 1.

Note: The clustering of dots about the horizontal levels is due to the difficulty of adequately scattering the individuals from unit groupings into a continuous distribution for texture score.

scatter diagram for the combination of the six years into one group is presented in Figure 2. These diagrams give information concerning the relationship which is not discernible from the constants usually calculated. The striking feature is the triangular nature of the swarm, shown to better advantage in Figure 2 where the full number of individuals are assembled. The empirical regression lines show fairly satisfactory agreement with the theoretical straight lines except for high protein flours in Figure 2. The latter discrepancy is probably due to disorderly differentiation of the crop seasons. Within any one season it seems reasonable to conclude that the regression is essentially linear. However, while flours of low protein content give rise to loaves with crumb textures varying all the way from "very poor" to "excellent," flours of high protein content give rise only to loaves of the best crumb texture. This is a very important characteristic. The suggestion that crumb textures may simply reflect the fermentation tolerance of the doughs under a "constant" baking procedure follows as a logical explanation, and incites a desire to see further investigation of the relationship between fermentation tolerance, percentage protein in flour and texture score.

Summary

Loaf volumes for hard red spring wheats of the 1921 to 1926 crop seasons have shown a small but positive correlation with crumb color and texture scores at the Minnesota State Testing Mill. This appears to be entirely due to the mutual relationship of crumb characters with protein content of the flour, the latter being positively correlated with loaf volume.

Color and texture of the crumb show a positive correlation with each other which is independent of the relationship of each to protein in the flour.

Neither ash in wheat or straight grade flour, diastatic activity of the flour, nor moisture content of the wheat appear to bear any relationship to crumb color.

Scatter diagrams of the relationship between crumb texture and protein content of the flour indicate that while there are flours of all protein contents that show the best texture standard, only low protein flours show individual samples of poor texture. The swarm is entirely triangular in nature, but the regression remains essentially linear within the individual crop seasons.

The studies reported here are based upon tests of straight grade unbleached flour. The conclusions drawn are not necessarily applicable to other flour grades, or to a composite group of flours of different grades.

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THE DETERMINATION OF ACIDITY IN FLOURS

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In spite of the many tests which have been made relative to the acidity of flours, there seems, as yet, to be but little agreement as to the proper method to use. Even the word "acidity" is not a fixed term, sometimes being used with regard to the hydrogen-ion concentration of the flour extract or suspension, and at other times with respect to the titer of such suspensions or extracts against alkali.

Many workers have proposed methods for the determination of titratable acidity of flours or meals among whom may be mentioned Ladd (1909), White (1909, 1912, 1915), Swanson (1912, 1915), Besley and Baston (1914), Barnard (1917), LeClerc (1920), and Hertwig (1926). Numerous comparative tests have likewise been undertaken. Among the most recent of these are the works of Bailey (1930), Brooke (1929), Collatz (1929, 1930), Fifield and Bailey (1929), Markley and Bailey (1931), and Johnson and Green (1931). The conclusions to be drawn from all of these comparative tests are, that no two tests will give corresponding results.

The whole problem is not made any easier when different operators express their results sometimes in degrees and at other times in per cents of lactic or sulphuric acid. On this point, as our knowledge of the character of the acidity in flour is limited, it would seem that we are only inviting further confusion when using the names of acids which we know that flour does not normally contain. It would appear, therefore, that an expression of titratable flour acidity simply as the volume of standard alkali necessary to neutralize a certain amount of flour, in which statement nothing is said about the nature of the acidity found, would be the preferable one.

It seems agreed amongst the majority of those making flour acidity tests that the term "acidity" should represent the acidity of the dry flour and not include the acids which form in a water suspension by the action of enzymes, bacteria, etc.

The simplest method for determining the nature of these acids, of course, would be a direct titration of a fresh flour suspension. This method is used to some extent in some parts of Europe, and being only an approximate method it has not gained much attention. With this

method, in order to get the flour properly in suspension, it is usually stirred with a little alcohol or acetone before adding the water.

Most other methods operate on the principle of extracting the acids before titration, using for this purpose, water and different organic solvents, as well as different temperatures and times of extraction. Among the better known may be cited the A. O. A. C. method, extracting for an hour with water at 40° C.; and the Greek or Balland method, using 85% alcohol at room temperature.

Before passing in judgment between these methods, it may be useful to consider what is known about the nature of flour acidity. It has been the classic idea that the acids in flour should be derived from the phosphoric compounds of the flour. This is but partially true. Most of the phosphorus appears tied up in phytin, from which soluble phosphates are split off by hydrolysis. These phosphates, however, form but a smaller part of the acidity. In a recent work Johnson and Green (1931) have pointed out that the increase in flour acidity on storage is due to organic acids of a fatty character, and that such acids, therefore, are responsible for increases in flour acidity. In addition, there may be small quantities of other alkali reactive substances, such as amino acids.

Experimental

The red color obtained by the titration of a fresh flour suspension against phenolphthalein disappears very rapidly. This is the chief cause of the inaccurateness in the suspension method, as the rate of titration applies to it a great subjective factor. If the suspension is left over night before titration, however, the color will keep fairly well.

When a flour suspension is allowed to rest with antiseptics added (0.5 of 1.0% formaldehyde is sufficient to prevent bacterial action) the acidity does not rise above a certain level. This increase in acidity continues very regularly, developing somewhat faster at higher temperatures. However, the upper limit will always be the same. What is more interesting is that the amount of soluble P_2O_5 increases proportionally with the acidity, and this development of soluble phosphates is a regular chemical process appearing in all flours, independent of the development of acidity by fermentation. To illustrate this point three suspensions were made of the same flour, and kept at 30° C. The following data were secured:

Suspension	Soluble P_2O_5 end of 24 hrs.	Acidity end of	
		24 hrs.	48 hrs.
	mgs.	cc. N/10 alkali	cc. N/10 alkali
No antiseptics	29.6	16.0	30.5
0.5% formaldehyde	29.1	6.2	6.5
1.0% formaldehyde	29.6	6.4	6.6

Acidity was titrated in the suspension, and expressed as cc. of N/10 alkali per 10 grams of flour; P_2O_5 is expressed in milligrams per 10 grams of flour. Suspension No. 1 showed evidences of strong bacterial action and gas development. However, as little as 0.5 of 1.0% of formaldehyde prevented this. Neither the formaldehyde nor the bacterial action influenced the solubility of the phosphates.

As previously mentioned, this reaction is a feature typical of all flours; at least it has been reproduced in all the flours examined by the author. When bacterial action is prevented it must follow that the increase in soluble phosphates is directly responsible for the increase in acidity, and undoubtedly also for the increase in electric conductivity, which has been reported by several investigators. An example of the reaction picture for two rye flours is shown in Figure 1. It is interesting to observe that the curves reproduced are of the general type of a unimolecular reaction. The process may be explained as a mere diffusion phenomenon, or it may be a real chemical reaction between phytin and water, which will be pseudo-unimolecular, the concentration of water being so large that it may be considered constant. Which of these theories is to be preferable, we are not as yet able to say.

An examination of the curve in Figure 1 will explain the rapid disappearance of the red color when titrating a fresh flour suspension, and also why, in an old suspension, the color will remain. Further, from the curve, it becomes clear that when a flour is extracted with water at 40° C. for an hour, according to the A. O. A. C. method, the extract will contain, chiefly, phosphates formed during the extraction time and not the acids present in the dry flour. These findings are in substantial agreement with those of Fifield and Bailey (1929), and Markley and Bailey (1931). As the fatty acid content of flour will hardly be soluble to any extent in water, the A. O. A. C. method accordingly cannot give a true picture of the acids preexisting in flour. During the investigations reported here it was found that the addition of a small quantity of alcohol to a flour suspension prevented the formation of soluble phosphates. This can be seen from the data given below. Portions of the same flour were suspended in water-alcohol of different concentrations and allowed to stand for 24 hours at 25° C.; the acidity in the suspension was then titrated and soluble P_2O_5 determined in the filtrates.

Alcohol per cent by volume	Acidity cc. $\frac{N}{10}$ alkali	P_2O_5 mgms.
8.0	5.2	22.12
12.0	4.0	13.17
24.0	3.3	4.8

Therefore, with those methods operating on the basis of extraction, no phosphates will be formed in addition to those already present in the dry flour. The question at once arises whether these phosphates are soluble, for instance, in the strong alcohol used in the Greek method.

Further examinations have confirmed this doubt. The consideration of flour acidity being put together from at least two components

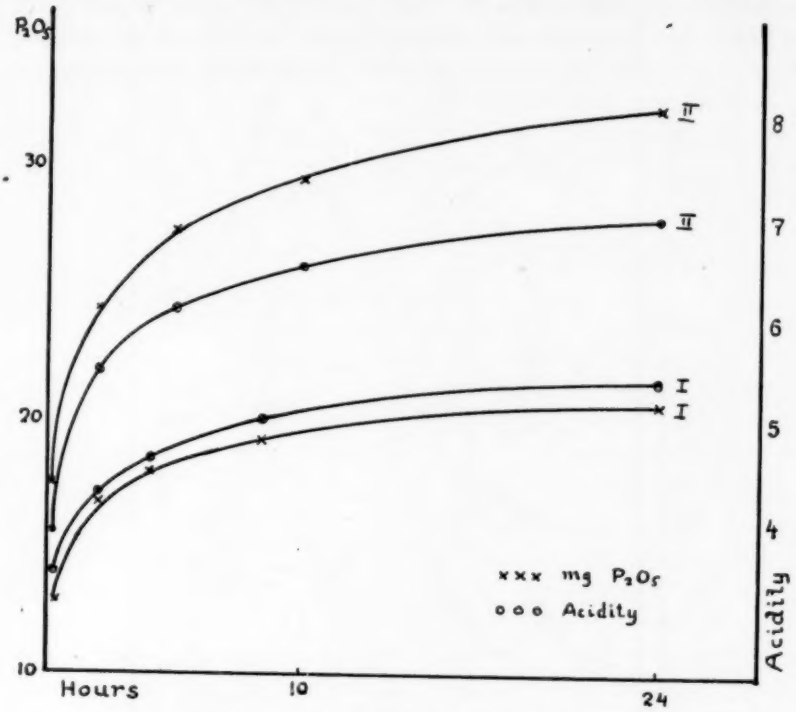

Fig. 1. Diagram showing increase in acidity and soluble P_2O_5 in flour-in-water suspensions.

made it important to know which concentration of alcohol would be most fit for solving them both. The procedure was as follows:

Ten grams of flour were stirred with the alcohol mixture, shaken thoroughly, and made up to 100 cc. After filtering, aliquots of the filtrates were titrated against N/10 alkali using phenolphthalein as indicator. The results obtained with four flours are reproduced graphically in Figure 2. These flours were: (1) Rye flour, rather old with high acidity; ash, 0.67%; poorly milled, containing many branny particles. (2) Rye flour from a modern mill; ash, 0.71%; acidity, normal. (3) Buffalo patent flour; ash, 0.48%; acidity, normal. (4) Clear flour; ash, 1.14%. It will be seen from the curves shown in Figure 2 that all flours developed maximum acidity at an alcohol concentration between 65% and 70%. This was also found to be true

from an examination of several other flours. It was decided, therefore, that this concentration of alcohol would be the proper one to use for the determination of flour acidity.

The simplest explanation for this phenomena must be that at the specified alcohol content the component parts, which unite to give the acidity values, are working together under the best conditions for

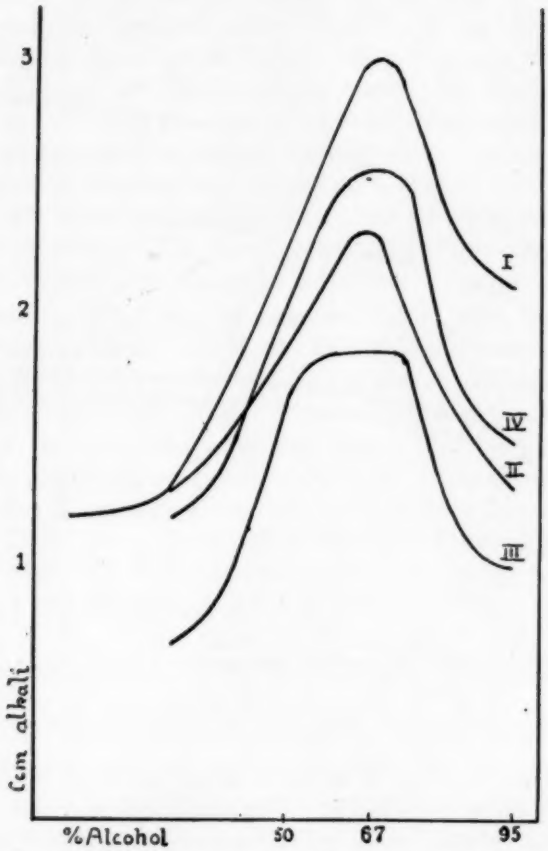

Fig. 2. Quantities of flour acidity extracted with different concentrations of alcohol.

solution. In attempting to confirm this theory further experiments were made.

Various concentrations of strong alcohol were stirred with solid KH_2PO_4 until saturated. The solution was filtered and the quantity which had dissolved in 10 cc. of the filtrate was titrated. In the same manner dilute alcohol mixtures were saturated with fatty acids which had been saturated from a neutral fat. The results are reproduced in Figure 3. If *a* milligrams of phosphate are present they will

readily dissolve in a fixed volume of alcohol below a certain concentration, let us say, 75%. The titer consequently forms a straight line through several concentrations. Above 75%, however, only so much phosphate will dissolve as it takes to saturate the liquid. This quantity decreased with increasing concentration of alcohol. In the same way *b* milligrams of fatty acids will behave towards diluted alcohol.

If the curves thus obtained are added, that is, if both phosphate and fatty acids are present at the same time, the resultant curve will resemble pretty well those found experimentally in flours.

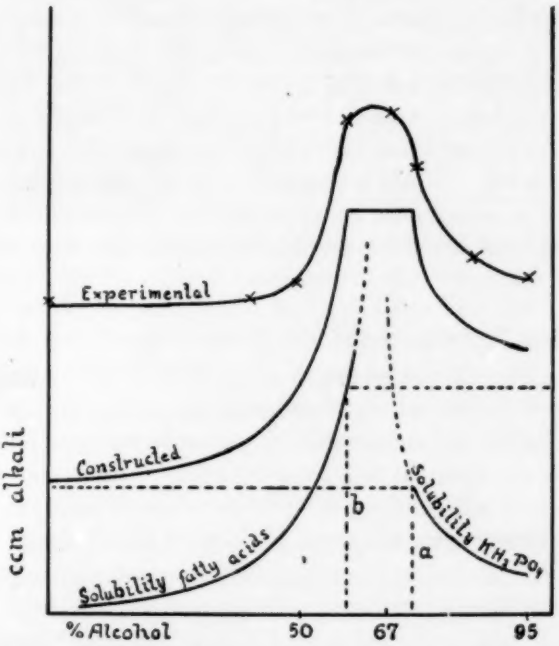

Fig. 3. Solubility of fatty acids and KH_2PO_4 in different alcohol concentrations. Titer curves, experimental and constructed from the solubilities.

For further verification 100 grams of wheat starch were added to 0.5 gram of KH_2PO_4 and one gram of fatty acids. The mass was sifted several times in order to insure thorough mixing. The mixture was then extracted and titrated and the acidity determined in different concentrations of alcohol, i.e., as was done with the flours. The titer curve, the upper one in Figure 3, is precisely of the same type as that constructed from the solubility studies.

Also, if small quantities of acids are present, they will be completely dissolved within wider concentration limits than large quantities. Thus, in a patent flour, containing a small amount of fatty material, the titer should be a constant during a marked interval. In fact, for

the patent flour figures reproduced in Figure 2, the upper part of the curve approaches a straight line.

These considerations should give sufficient evidence that flour acidity, as a function of the alcohol concentration of the extraction medium, is, to a great extent, a question of solubility. Consequently it should be correct to extract with that alcohol solution which is most effective for dissolving the component parts which together are responsible for flour acidity, i.e., 67% alcohol instead of 85% alcohol as recommended in the Greek or Balland method.

It is possible also that even this concentration is not able to dissolve all of the acids present. As already stated by Johnson and Green (1931), there is a great difference between the acids extracted by ether and the acids extracted by 85% alcohol. Some of this difference must be due to phosphates, and the rest probably to acids of amino acid character. As yet we know but very little about this third component part of flour acids. From a consideration of the solubility of gluten in alcohol, it is reasonable to suppose that a concentration of 67% alcohol would be a favorable one for dissolving this component part of flour acidity also.

Method Recommended For Determining Flour Acidity

The extraction of the acids from a flour with 67% alcohol is a very rapid operation. The acids go into solution easily and the liquid filters rapidly. In order to make sure of the time necessary for complete extraction of the flour acids, portions of the same flour were mixed with alcohol and let stand for different periods of time before filtering. The results obtained working at 25° C. were as follows:

Time of extraction Hours	Acidity cc. $\frac{N}{10}$ alkali
Filtered at once	3.95
1	4.00
2	3.90
3	3.90
4	3.90

Another series of tests made at 15° C. gave practically the same results. Consequently, a long period of extraction is not necessary. On the contrary, it is somewhat of a drawback, as it makes liquid filter more slowly. The extraction can be made at room temperature. The most practical manner of making the test is described below:

Ten grams of flour are suspended in 67% alcohol, made to a volume of 100 cc., shaken vigorously for some minutes and filtered. An aliquot of the filtrate is titrated against N/10 alkali using phenolphthalein as

the indicator. The acidity is expressed as cc. N/1 alkali per 100 grams of flour or cc. N/10 alkali per 10 grams.

The results obtained in this way are somewhat higher than those obtained by the Greek method and there does not seem to be any constant ratio between the two methods. Likewise, they will not correspond with the A. O. A. C. method. On the other hand, however, they are in good agreement with the results obtained by directly titrating a fresh flour suspension when the titration is done by an experienced operator. The following data are given to demonstrate this:

Kind of flour	Suspension method	Extraction method
	cc. N/10 alkali	cc. N/10 alkali
Old rye flour	3.60	3.90
Rye flour	2.70	2.80
" "	2.95	3.00
" "	2.50	2.60
Patent wheat flour	1.90	2.10

If the reasoning is correct, that the acids present in the dry flour can be titrated directly in a fresh suspension, the concordance in results between the two methods gives further proof for the opinion that titration of a 67% alcoholic extract of the flour gives the most nearly correct picture of the acids originally present. The experiments just cited here have been repeated with both rye and wheat flours of different grades, and they demonstrate the general reliability of the method.

Summary

(1) Flour acidity should always mean the acids present in the dry flour. These acids are partly phosphates, partly fatty acids, and possibly some amino acids and protein matter. (2) The acidity of a flour suspension containing antiseptics increases regularly up to a certain limit which is not exceeded. This rise in acidity is proportional to the increase of soluble phosphates, which are formed from organic phosphoric compounds by the action of water. (3) In consideration of the statement made in item 2, the A. O. A. C. method gives incorrect results as it extracts phosphates not originally present as such. (4) It was shown that in alcoholic solutions no phosphates will be formed in addition to those already present in the flour. On the contrary the original phosphates are not completely soluble in 85% alcohol and, therefore, the Greek method will give too low results. (5) Both phosphates and the fatty acids are easily soluble in 67% alcohol, which seems to be the proper concentration for the extraction of flour acids. (6) That the extraction of flour acids is largely a question of solubility was shown experimentally. (7) A method for determining flour

acidity by extraction with 67% alcohol is described. The results thus obtained corresponded quite well with acidities found by direct titration of flour suspensions.

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SOME FACTORS IN FERMENTATION TOLERANCE [1]

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Introduction

The meaning and determination of fermentation tolerance have been the subject of discussion by various workers. The term as commonly used means the range in the time of fermentation under which a flour will make good bread. The harm to bread from too long a period of fermentation is due to at least three factors—sugar exhaustion, physical effects on the dough, and accumulation of by-products. The latter includes lactic and acetic acids, and alcohol, as well as some substances very imperfectly known. Harrel (1926) found that the fermentation periods of both sponge and straight doughs could be varied only slightly and still produce loaves having desirable characteristics. Bailey and Johnson (1924), and St. John and Hatch (1931), found that the fermentation range could not exceed 50 to 80 minutes on the flours they studied. Moen (1930), reported the effects of various fermentation periods. Jørgensen (1931) emphasized the importance of separately examining "strength" and "gassing power." Working (1929) emphasized the need of dividing the factors of fermentation tolerance into those affecting the rate of gas production and the dough rise with consequent oven spring.

It is often assumed that a low fermentation tolerance in a flour is due to a minimum of yeast food material. The diastatic or saccharogenic activity of a flour has been closely correlated with loaf volume and color by Bailey (1925). Blish and Sandstedt (1927) state: "Fermentation tolerance or stability as ordinarily regarded from the production view-point, is an item which is associated more closely with the factor of gas production than gas retention. That is to say, that with yeast constant, diastase or sugar is the determining factor rather than gluten quantity or quality, as is frequently the case." In view of the above findings, Blish, Sandstedt, and Platenius (1929) state: "This is doubtless an important reason why the sponge dough method of bread making (in which sugar is incorporated almost immediately preceding panary fermentation) is more fool-proof than the straight dough method. When handled by the straight dough method flours

[1] Contribution No. 42, Department of Milling Industry.

vary widely as to their relative fermentation tolerance." Also, "If it is true that fermentation tolerance depends more upon sustained gas production than upon gluten quality, it follows that variations in fermentation tolerance must be proportioned to corresponding variations in diastatic power."

It was felt by the authors that further information on this subject could be secured if a satisfactory method could be devised for supplying the yeast with food materials without materially altering the physical character of the dough. This would make it possible to supply yeast food at various stages during the dough fermentation and to observe the effect of such additions.

Experimental Procedure

Mixing and breaking procedure. The Swanson type of mixer which has been recognized by Heald (1930), and by Merritt and Blish (1931), as accomplishing an efficient and thorough mixing in a minimum of time was used. For squeezing out the gas and otherwise mechanically affecting the dough at the different stages of fermentation, a dough break was used. This was designed by E. B. Working and made from two 6″ × 12″ smooth rolls. The dough squeezing studies were included because it is well known in commercial practice that an overfermented dough may be "brought back" if subjected to the dough break.

Flour used. The flour was milled from a Kansas hard winter wheat of known baking characteristics.

Baking procedure. A standard dough was made from the following ingredients:

Flour	500	grams
Sugar	20	grams
Salt	9	grams
Shortening	7.5	grams
Water-for proper absorption		

The dough was subjected to mixing and dough breaking at various stages during the fermentation periods.

The ingredients were mixed for one minute at medium speed (80 r.p.m.) on the Swanson type of mixer, and the dough divided into two equal parts, making each loaf equivalent to 250 gms. of flour. The doughs were then allowed to ferment for 90 minutes, followed by punching, sometimes also by breaking after one or more 40-minute or other intervals, molded and proofed to constant volume, and baked at 230° C. for 40 minutes. The temperature of the fermentation and proofing cabinet was maintained at 32° C. The loaves were baked in special

aluminum cylindrical baking pans in use in this laboratory (Swanson et al., 1915; and Hanson, 1931).

Method of scoring loaves. After cooling, usually the following day, the volumes were measured and the loaves were judged for texture and crust color. The texture was rated according to the following scheme:

Score	Characteristics
99 to 100	very excellent texture, silky, long fibers
97 to 98	very good texture
95 to 96	good texture
93 to 94	fair
91 to 92	poor
90 or below	very poor

Baking Value. In order to make it easier to compare the loaves from the various bakings with each other, arbitrary baking values were computed from the loaf volumes and texture scores for the loaves from 250 gms. of flour in the following manner: (1) Subtract 1000 from loaf volume and divide by 12; (2) subtract 80 from texture score and multiply by 2.5; and (3) add the two values. To illustrate:

Loaf volume 1580. $1580 - 1000 = 580$, $\div 12 = 48$.
Texture 96. $96 - 80 = 16$, $\times 2.5 = 40$.
Baking value $(48 + 40) = 88$.

Effect of Remixing and Use of Dough Break

One series of tests was planned to determine the effect of remixing the dough for one minute as well as using the dough break after the dough had been fermented for two or more periods. The data obtained are given in Table I. The figures under "scheme" stand for minutes of fermentation time, the dough being punched between each period; "m" means mold and place in pan; "p," proof; "db," dough break, or passing the dough between the rolls several times; and "mix," remixing the dough with additional ingredients. The punching was done by passing the dough through the dough break once and then forming in the hands. A separate experiment showed that more uniform results could be obtained by this method than by punching with the hand. The procedure may be better understood by considering a typical loaf, "*D*-4," treated according to the scheme, 90–40–40–40–40–mix–db–m–p. The figures mean: After mixing the dough it was allowed to ferment for 90 minutes, then punched, after which it was allowed to ferment for four additional 40-minute periods with a punch at the end of each period, after which it was placed in the mixing bowl and mixed for one minute at slow speed, passed through the dough break several times, molded, placed in the baking pans, proofed to constant volume, and then baked.

The figures in Table I show the following: (1) Prolonged fermentation decreases the loaf volume and lowers the texture score as would be expected (see series A). (2) Using the dough break before the last

TABLE I

EFFECT OF REMIXING THE DOUGH AS WELL AS USING THE DOUGH BREAK AFTER FERMENTATION

Loaf number	Loaf volume cc.	Texture Score	Baking value Score	Scheme [1]
	A. Effect of fermentation time on volume and texture			
A–1	1775	96	107	90–40–m–p.
A–2	1645	97	96	90–40–40–m–p.
A–3	1630	97	95	90–40–40–40–m–p.
A–4	1605	94	86	90–40–40–40–40–m–p.
	B. Effect of dough break before molding and proofing			
B–1	1695	95	97	90–40–db–m–p.
B–2	1720	98	107	90–40–40–db–m–p.
B–3	1660	98	101	90–40–40–40–db–m–p.
B–4	1645	94	90	90–40–40–40–40–db–m–p.
D. Effect of one minute slow speed remixing and dough break before molding and proofing				
D–1	1665	98	101	90–40–mix–db–m–p.
D–2	1695	98	104	90–40–40–mix–db–m–p.
D–3	1730	98	108	90–40–40–40–mix–db–m–p.
D–4	1650	94	89	90–40–40–40–40–mix–db–m–p.
E. Effect of one minute slow speed remixing and no dough break before molding and proofing				
E–1	1710	95	98	90–mix–40–m–p.
E–2	1620	96	92	90–40–mix–40–m–p.
E–3	1535	92	74	90–40–40–mix–40–m–p.
E–4	1560	94	82	90–40–40–40–mix–40–m–p.
	F. Effect of remixing and dough break before last fermentation period			
F–1	1815	96	111	90–mix–db–40–m–p.
F–2	1725	97	104	90–40–mix–db–40–m–p.
F–3	1685	97	101	90–40–40–mix–db–40–m–p.
F–4	1620	94	88	90–40–40–40–mix–db–40–m–p.

[1] See text for explanation of terms.

punch, molding, and proofing minimizes the injuries from the long fermentation (compare series *A* and *E*, with *B*, *D*, and *F*). However, when the fermentation has gone too far, as shown by the last loaf in each series, the dough break does very little good. (3) Remixing after one or more periods of fermentation has a harmful effect on the volume and texture (compare series *A* and *E*). This may be remedied by the dough break (compare series *A* and *D*). This shows that yeast food may be mixed with the dough after several periods of fermentation without any serious effects from the mixing. (4) One fermentation period after the dough break seems to have very little effect (compare series *D* and *F*).

Effect of Adding Starch

When doughs were fermented for 12 hours or more, the accumulation of water caused the dough gradually to become so slack that it became very difficult to handle. To overcome this, corn starch was added to the dough in sufficient quantity to make it stiff enough to handle. In order to be certain that the starch did not furnish yeast food and thus invalidate some other factors that were being measured, one series of loaves was baked to which starch was added in amounts sufficient to make a dough of usual stiffness; and another series to which both starch, in the same amounts as in the other series, and 10 grams of sugar were added during the fermentation period. Table II shows the results obtained. The added starch did not seem to have any noticeable effect on either the loaf volume or texture.

TABLE II

EFFECTS OF THE ADDITION OF STARCH

Loaf number	Loaf volume cc.	Texture Score	Baking value Score	Treatment with starch gms.
	A. 12 hours—mix starch—(40)$_2$–db–m–p.			
52	1100	84	18	0
53	1115	84	20	5
54	1160	84	23	10
55	1160	84	23	20
56	1165	84	24	30
57	1160	84	23	40
	B. 12 hours—mix starch and 10 gr. sugar—(40)$_2$–db–m–p			
58	1620	94	87	0
59	1700	94	97	5
60	1650	94	90	10
61	1630	94	88	20
62	1675	94	93	30
63	1660	94	91	40

Effect of Dough Break

Since it was found that less injury was produced by the longer periods of fermentation if the dough was passed through the dough break, it seemed advisable to determine the number of times that a dough could be passed through this machine without serious injury. Apparently the dough break serves to remove some of the products of fermentation, particularly carbon dioxide, and to reunite broken gluten strands. Table III shows some of the results obtained. It seems that doughs fermented for 3½ hours are injured markedly in texture and volume by passing through more than two times. If, however, the doughs have been fermented for more extended periods, injury is less marked by passing several times. If old dough is not passed

through the dough break at all, the loaf has an "old" appearance; but passing through the dough break many times has a very harmful effect even to long fermented dough.

TABLE III

EFFECT OF THE DOUGH BREAK

Loaf number	Loaf volume cc.	Texture Score	Baking value Score	Scheme	Treatment
36	1670	96	97	90–$(40)_3$–db–m–p.	No dough break
37	1740	97	106	"	2 times through dough break
38	1650	93	87	"	5 " " " "
39	1600	92	80	"	10 " " " "
40	1580	89	70	"	15 " " " "
41	1540	89	67	"	20 " " " "
42	1490	88	61	"	30 " " " "
43	1490	88	61	"	40 " " " "
44	1540	91	72	12 hrs.–mix–sugar $(40)_3$–db–m–p.	No dough break
45	1705	97	103	"	2 times through dough break
46	1635	98	99	"	5 " " " "
47	1550	97	88	"	10 " " " "
48	1520	96	83	"	15 " " " "
49	1420	91	62	"	20 " " " "
50	1360	88	55	"	30 " " " "
51	1405	88	54	"	40 " " " "

Effect of Adding Sugar at the Time of Remixing

In one series of experiments 10 grams of sucrose were added when the dough was remixed in order to note the effect of adding this yeast food constitutent after various periods of fermentation. Typical

TABLE IV

EFFECT OF ADDING SUGAR ONE OR MORE TIMES WHEN DOUGH WAS REMIXED

Loaf number	Loaf volume cc.	Texture Score	Crust color Score	Baking value Score	Scheme
	A. Effect of prolonged fermentation without additional sugar				
1	1360	96	97	70	90–m–p.
2	1400	97	97	76	90–40–m–p.
3	1380	98	96	77	90–40–40–m–p.
4	1340	90	85	53	90–40–40–40–m–p.
5	1140	85	85	25	90–40–40–40–40–m–p.
6	1020	80	85	2	90–40–40–40–40–40–m–p.
	B. Effect of adding sugar at the time of remixing				
7	1580	97	98	91	90–90–mix–40–40–db–m–p.
8	1550	97	98	89	90–90–mix–90–90–mix–40–40–db–m–p.
9	1520	97	98	86	90–90–mix–90–90–mix–90–90–mix–40–40–db–m–p.
10	1600	98	98	95	90–90–mix–90–90–mix–90–90–mix–90–90–mix–40–40–db–m–p.

results are given in Table IV. As will be seen from the scheme, loaves 7, 8, 9, and 10 were fermented for 4½, 7½, 10½, and 13½ hours, respectively; and sugar was added one, two, three, and four times, respectively. The figures and photo show that without additional sugar two 40-minute periods after the preliminary 90 minutes give the best baking results. However, when additional sugar was mixed with the dough, good volumes and textures were obtained after 4½, 7½, 10½, and 13½ hours of fermentation, respectively, the longer fermentation time having no more injurious effect than the shorter. The crust color showed that the sugar was not exhausted. The bread from the long fermentation periods, however, had a sour taste.

Time Required to Exhaust Sugar Added to Excessively Over-Fermented Dough

Several trials had shown that the 10 grams of sugar added to the dough formula would be consumed in approximately 3 hours when the dough was fermented at 32° C., and approximately twice that time was required to consume 20 grams of sugar. In one series of experiments 10 and 20 grams of sugar, respectively, were added to various doughs each fermented for 12 hours, then these doughs were fermented respectively for 1, 3, 5, 7, 9, and 12 additional 40-minute periods, punching between each. The results are given in Table V. The 10 grams of sugar added at remixing was exhausted soon after 5, 40-minute periods, while the 20 grams were exhausted soon after 9, 40-minute periods. This means that fermentation time was closely related to the amount of sugar available in the dough. The results also show that good color, volume, and texture may be obtained from a dough fermented

TABLE V

EXHAUSTION OF SUGAR FROM OVER-FERMENTED DOUGH

Loaf number	Loaf volume cc.	Texture Score	Crust color Score	Baking value Score	Scheme
			10 gms. sugar added at mix		
64	1590	92	98	79	12 hrs.–mix (40)–db–m–p.
65	1630	96	95	93	12 " " $(40)_3$–db–m–p.
66	1560	92	88	77	12 " " $(40)_5$–db–m–p.
67	1150	80	88	12	12 " " $(40)_7$–db–m–p.
68	1120	80	88	10	12 " " $(40)_9$–db–m–p.
69	1100	80	88	8	12 " " $(40)_{12}$–db–m–p.
			20 gms. sugar was added at mix in this series		
70	1630	98	98	98	12 hrs.–mix (40)–db–m–p.
71	1740	98	98	109	12 " " $(40)_3$–db–m–p.
72	1680	96	98	98	12 " " $(40)_5$–db–m–p.
73	1560	92	95	77	12 " " $(40)_7$–db–m–p.
74	1670	92	88	77	12 " " $(40)_9$–db–m–p.
75	1150	80	88	12	12 " " $(40)_{12}$–db–m–p.

12 hours by adding sugar, remixing, then fermenting for several periods using the dough break and then proofing. The bread in all cases was sour, but the development of acid did not seem to inhibit the formation of good texture, color, and volume as long as available sugar was present.

Effect of Adding Lactic Acid

Since lactic acid is one of the products developed during fermentation, to what extent is the accumulation of this substance a factor in fermentation tolerance? Three series of doughs *A*, *B*, and *C* were fermented for various fermentation periods and then lactic acid (sp. gr. 1.2) was added in varying amounts just before the last 40-minute fermentation period. The results are given in Table VI.

A small amount of added lactic acid seems to benefit the loaf volume and texture, but beyond 0.5 cc. it becomes harmful, and this was more pronounced with the doughs fermented the longest. Loaves in series

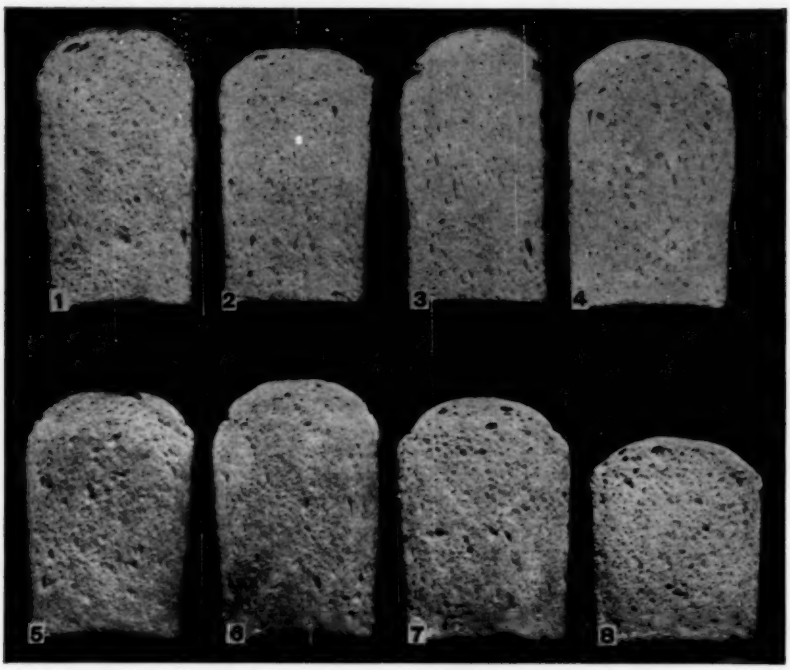

Fig. 1. Typical results obtained in several experiments.

Loaf number	Fermentation time	Supplementary sugar
1	4 hr. 20 min.	Sugar added at end of 3 hr.
2	7 " 20 "	" " " " " 3 & 6 hr.
3	10 " 20 "	" " " " " 3, 6, & 9 hr.
4	13 " 20 "	" " " " " 3, 6, 9, & 12 hr.
5	1 " 30 "	No additional sugar
6	3 "	" " "
7	4 " 30 min.	" " "
8	6 "	" " "

C show very beneficial results of mixing sugar with the over-fermented dough. Since these doughs after such a long period of fermentation contained considerable amounts of lactic acid, and since the addition of a small amount did not seem harmful, it would appear that it is not the acid itself, as developed during fermentation, that is most harmful to the volume and texture. In Figure 1 are shown typical loaves obtained in the several experiments just discussed.

TABLE VI

ADDING LACTIC ACID TO OVER FERMENTED DOUGH

Loaf number	Loaf volume cc.	Texture Score	Baking value Score	Lactic acid added cc.
		A. 90–40–mix acid 40 db–m–p.		
11	1575	91	75	0.0
12	1655	97	98	0.25
13	1675	97	101	0.50
14	1560	92	85	1.00
15	1375	88	51	1.50
		B. 90–40_s–mix acid–40–db–m–p		
16	1520	91	72	0.0
17	1585	94	83	0.25
18	1595	96	89	0.50
19	1505	93	77	1.00
20	1370	88	51	1.50
		C. 12 hrs.–mix sugar–40–mix acid–40–db–m–p.		
21	1700	97	102	0.0
22	1710	98	106	0.25
23	1610	97	93	0.50
24	1630	92	83	1.00
25	1520	89	65	1.50

Conclusions

Since the authors used a strong flour the conclusions are limited to this fact. When the fermentation of a dough is prolonged beyond the normal optimum fermentation period, the volume and texture of the bread produced is markedly decreased even if sufficient sugar is present in the dough. The proper use of the dough break helps to overcome the injury due to over-fermentation even when this is very severe (Table I).

Lack of sugar in the dough during the proofing period, prevents the production of good volume and texture, and if the prolonged fermentation has exhausted the sugar in the dough, more sugar must be added before good volume and texture will be produced even with the use of the dough break.

Injury to the physical properties of the dough due to over-fermen-

tation is aggravated by the remixing necessary in the incorporation of more sugar, but this may also be corrected by the dough break.

The effects of lactic acid, which is one of the by-products of fermentation were not conclusive.

Repeated rise and punchings of the dough seems to separate the gluten strands in such a way that they do not form the numerous cells for the retention of the gas necessary for good texture. When the dough is squeezed as in the dough break, these gluten strands are reunited as in freshly mixed dough. Such treatment of old doughs helps to produce the fine texture obtained in bread from properly developed dough.

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THE RELATION BETWEEN TOTAL PROTEIN, PEPTIZABLE PROTEIN, AND LOAF VOLUME AS OBTAINED BY SUCCESSIVE INCREMENTS OF POTASSIUM BROMATE

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Introduction

The advisability of introducing oxidizing agents into the baking formula to insure the development of the full potentialities of flour with respect to loaf volume and other loaf characteristics has been discussed by previous investigators. Herman and Hart (1927) pointed out the advantages to be derived by the use of 0.5 gm. of a certain yeast food or 0.001% of $KBrO_3$ in the baking formula. Herman (1927) further stated that the use of the differential baking test materially widened the application of the experimental milling test. Werner and Herman (1928) in discussing the differential baking test stated that flours which were non-responsive to $KBrO_3$ would be found lacking in commercial usage in, what is termed by the practical baker, strength or stability.

Blish and Sandstedt (1927) in discussing the differential baking test, especially with respect to the use of oxidizers in the baking industry, considered that the response of an untreated flour to the presence of an oxidizing agent as strongly indicative of the oxidation tolerance of the original wheat. Although not presenting data to demonstrate the point, Blish and Sandstedt further stated that the tolerance of flours towards oxidizing agents is roughly proportional to their protein content. When testing experimentally milled flours, however, these investigators recommend the use of 5% of sugar in the test formula to compensate for the lack of diastatic activity in such flours. Blish (1928) again discussing the differential baking test concluded that the practical utility of such a test was sufficient recommendation to include it as "supplementary test C" of the Standard Experimental Baking Test of the A. A. C. C.

Bailey (1930), summarizing his report as Chairman of the 1930 Experimental Baking Test Committee, stated: "The A. A. C. C. Baking Procedure with supplement C (addition of bromate), emphasizes desirable characteristics or deficiencies in wheats which the Basic Procedure alone fails to reveal."

In Canada, likewise, evidence has been accumulated to show the value of the differential baking test. Larmour and MacLeod (1929) using a modified form of the differential baking test suggested by Werner (1925), and recommended by Blish (1928), found it particularly helpful in evaluating Canadian hard red spring wheats. These investigators also pointed out the advantages to be obtained when using the experimental baking test from the use of 3% of diastatic malt in combination with 0.5% of yeast food in distinction to the use of 1% of diastatic malt and 0.001% of $KBrO_3$. Later, Larmour (1930) used the differential baking test to justify the commercial use of the protein test as a factor in the classification of hard red spring wheats with respect to baking quality.

Working (1928) theorized with respect to the action of oxidizers in liberating phosphatide, and the resultant beneficial effect which phosphatides might have upon the tensile strength of gluten and the ductility of dough. He also considered the addition of an oxidizer to the baking test formula as desirable.

Experimental

The Problem. Although considerable investigation appears to have been published with respect to the action of various amounts of yeast foods and malt extracts, either singly, or in combination, on dough and bread characteristics, little published data appears to be available describing the effect of successive increments of $KBrO_3$ upon loaf volume and other bread characteristics. To determine the effect, particularly with reference to the relationship between loaf volume and the crude protein content of flour, a series of tests were carried out on a number of flours of diverse characteristics, as well as variable protein content. As a supplementary program, studies were also carried out to determine whether any significant relationship existed between peptizable protein and loaf volume as obtained by successive increments of $KBrO_3$.

Material. The flours used were milled from the 1930 Saskatchewan wheat crop, and included commercial, experimentally milled, and millstream flours. The protein content of these flours varied from 9.4% to 20.2%. At least one flour sample, No. 302, was milled from Garnet wheat and it is believed that one or two other flours were milled from wheat containing blends of Marquis and Garnet wheat. The millstream flours were included to secure flours of very high protein content. Since, in previous studies, the author (1930, 1931) found that the relations between crude protein content, protein peptizability, and loaf volume were essentially the same for commercially milled, experimentally milled, and millstream flours, the inclusion of data from these three classes of flour into one series could not be expected to

materially alter the conclusions to be drawn, so that the data from the three classes of flours have been analyzed as one.

Baking Tests. The baking tests were conducted according to those described by the A. A. C. C. (Blish, 1928), with these exceptions: Two gms. of salt were used in the formula instead of 1 gm. and water absorption was arranged to provide for proper consistency rather than a fixed absorption as recommended in the A. A. C. C. test.

When malt was used in the tests it was added in solution, 4 cc. of which contained 1 gm. of diastatic malt, and 3.3 cc. of water.

The $KBrO_3$ was added from a stock solution containing 1 gm. of $KBrO_3$ in 1000 cc. of water by means of a Mohr pipette. One to 4 cc. of bromate was used according to the concentration of improver desired.

Peptization Tests. The flours were extracted for one hour with distilled water, and 0.5N solutions of $MgSO_4$, NaCl, and KBr using the method previously described by the author (1931a). This procedure was found to compare favorably with the methods used by Gortner, et al. (1929), and by Geddes and Goulden (1930).

The Data

The earlier investigations of Herman and Hart (1927) as well as those of Larmour and MacLeod (1929) have demonstrated the stimulative effect of diastatic malt upon loaf volume. The literature just cited has served to illustrate the influence of small amounts of $KBrO_3$ on loaf volume. In order to determine what influence increasing amounts of $KBrO_3$ would have on loaf volume, on flours of different protein contents, with and without the presence of diastatic malt, a series of baking tests were undertaken in a preliminary way, on 4 flours having wide differences in protein content. This preliminary work was necessary on account of the fact that the supply of flours to make this study was limited and it was necessary to select a procedure which would bring about the most outstanding changes in loaf volume. The data from this preliminary experiment, given in Table I, demonstrates quite fully that the most outstanding differences were to be found in those tests made from the flours containing diastatic malt. Accordingly, this procedure was used on the 15 flours selected for study. The baking data resulting from this enlarged series of tests are shown in Table II.

These data show that with the lower protein flours, flours which contained from 9.4% to 11.0% of protein, there was a decreased stimulation in the matter of loaf volume, when more than 1 mg. of $KBrO_3$ was used. With the flours that ranged in protein content from 11.7% to 14.0% the effect of both 1 and 2 mgs. of bromate was closely the

TABLE I

COMPARATIVE LOAF VOLUMES OBTAINED BY INCREASING INCREMENTS OF $KBrO_3$ ADDED TO FLOUR WITH AND WITHOUT THE ADDITION OF 1% OF DIASTATIC MALT

Flour number	Crude protein of flour	Loaf volumes with indicated milligrams of $KBrO_3$								
		(with 1% malt)					(without malt)			
		(Basic) none	1	2	3	4	1	2	3	4
	P.ct.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
300	10.9	388	448	426	420	360	398	420	398	370
307	13.0	485	580	560	560	510	540	540	520	492
313	16.0	500	638	710	730	625	600	670	680	670
315	20.2	545	757	870	1000	850	632	733	880	870

TABLE II

COMPARATIVE LOAF VOLUMES OBTAINED BY THE ADDITION OF SUCCESSIVE INCREMENTS OF $KBrO_3$ TO 15 FLOURS OF WIDELY DIFFERENT BAKING STRENGTHS[1]

Flour number	Crude protein of flour	Ash content of flour	Loaf volumes with the indicated milligrams of $KBrO_3$				
			(Basic) none	1	2	3	4
	P.ct.	P.ct.	cc.	cc.	cc.	cc.	cc.
301	9.4	0.50	400	490	470	450	425
302[2]	10.4	.41	415	395	390	370	350
303[2]	11.0	.47	472	524	525	495	470
304	11.3	.31	450	510	530	480	480
305	11.7	.37	475	560	540	510	490
306	12.6	.32	480	565	575	560	525
307	13.0	.41	485	580	560	560	510
308	13.3	.52	485	525	525	510	488
309	13.8	.47	460	590	615	612	570
310	14.0	.62	475	585	590	560	530
311	14.7	.52	538	585	635	605	595
312	15.6	.43	485	700	700	680	600
313	16.0	.71	500	638	710	730	625
314	18.2	.46	520	712	825	845	740
315	20.2	.56	545	757	870	1000	850

[1] All data on a 13.5% moisture basis.
[2] Milled from musty wheat.

same, while a decrease in loaf volume below that obtained by the use of 1 or 2 mgs. of $KBrO_3$ took place on the addition of 3 and 4 mgs. of bromate.

The two flours, with protein contents of 14.7% and 15.6%, made increasingly large loaves as compared to the control with a concentration of 1 and 2 mgs. of bromate; while the very high protein flours, those containing 16.0%, 18.2%, and 20.2%, produced loaves increasing in size with concentrations as high as 3 mgs. of bromate.

The highest concentration of bromate used, 4 mgs., reduced the size

of the loaf below the control in only one instance, sample 302. In the tests with those flours varying in protein content from 9.4% to 15.6% there was an increase in the size of the loaf over the control, but of lesser sizes than that produced by the addition of either 1, 2, or 3 mgs. of bromate. The flours with the higher percentages of protein reacted most favorably to a concentration of 4 mgs. of bromate.

It would appear, therefore, that the use of higher concentrations of bromate would be justified in testing these flours, because of the greatly increased volumes which were obtained with the high protein flours. Flour No. 315, for instance, almost doubles the basic loaf volume when treated with 3 mgs. of $KBrO_3$. Flour No. 311 gave the second highest loaf volume when baked by the basic method, whereas, in reality, only fifth in point of strength.

The relation between protein content and loaf volume for each baking formula is expressed by the simple correlations given in Table III. The significance of these correlation constants may be judged by

TABLE III

CORRELATION CONSTANTS COMPUTED BETWEEN TOTAL PROTEIN AND LOAF VOLUME

Basic procedure	Bromate-malt procedure with indicated milligrams of $KBrO_3$			
	1	2	3	4
r_{ae} = +.8457	+.9191	+.9630	+.9652	+.9637

Value of r at 5% point, .5139
Value of r at 1% point, .6411

a = crude protein
e = loaf volume

Test for significance of differences in the correlation constants.

r	Z	$Z_1 - Z_2$	$\sqrt{Z_1 - Z_2}$	$\frac{Z_1 - Z_2}{\sqrt{Z_1 - Z_2}}$
+.8457 +.9630	1.2409 1.9856	.7447	.4082	1.82
+.8457 +.9191	1.2409 1.5803	.3394	.4082	0.83
+.9191 +.9630	1.5803 1.9856	.4053	.4082	0.99

comparison with the value of r at the 5% and 1% points, which have been inserted in the table. The significance of the difference in the pairs of correlations given just above the values for Z is measured by the Z tests of Fisher (1928). The significance of the difference between any two correlations may be expressed by the ratio of the difference in Z values $(Z_1 - Z_2)$, to its standard deviation $(\sqrt{Z_1 - Z_2})$. Since there are 15 pairs of variables involved in each of these correlations, the standard error of the difference in Z is $\sqrt{1/12 + 1/12} = .4082$. As the difference in the Z values in each case is not greater than twice

the standard error, these differences are not significant, and there is not a significant increase in the relationship between crude protein and loaf volume with 2 mgs. of $KBrO_3$. Therefore, it would not seem that the use of larger quantities of the reagent than are usually employed would result in a stronger relationship between crude protein and loaf volume.

Moreover, the correlation constants shown in Table III appear to be remarkably high when the varied character of the flours under test is taken into consideration. More so when the inclusion of several samples of somewhat doubtful soundness does not seem to have materially altered the relation between crude protein and baking strength.

Peptization Studies

The percentage of total protein extracted from these flours by various solvents is shown in Table IV. From the data presented here

TABLE IV

PER CENT OF TOTAL PROTEIN EXTRACTED BY VARIOUS SOLVENTS FROM WHEAT FLOUR.

Flour number	Crude protein of flour	Protein extracted as per cent of total by			
		H_2O	$\frac{N}{2}$ $MgSO_4$	$\frac{N}{2}$ NaCl	$\frac{N}{2}$ KBr
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
301	9.4	20.2	12.3	22.1	32.6
302	10.4	42.8	18.2	26.4	26.9
303	11.0	29.5	19.1	21.4	25.5
304	11.3	25.7	18.6	24.3	29.3
305	11.7	27.3	17.1	19.6	29.3
306	12.6	25.0	15.9	18.6	28.6
307	13.0	19.6	16.6	19.6	26.9
308	13.3	15.9	14.6	16.2	21.7
309	13.8	19.5	13.8	15.7	27.6
310	14.0	16.3	12.2	19.9	29.3
311	14.7	18.7	18.7	19.7	26.9
312	15.6	17.3	16.0	16.9	23.7
313	16.0	16.2	17.2	22.8	31.7
314	18.2	15.4	12.1	15.9	21.4
315	20.2	13.0	12.2	16.8	21.7
Average		21.5	15.6	19.7	26.9

it is evident that in 13 out of 15 cases distilled water extracted more protein from the flours than did $\frac{N}{2}$ $MgSO_4$, and more protein than $\frac{N}{2}$ NaCl in 7 out of 15 cases. With respect to flours Nos. 302 and 303, distilled water extracted a greater percentage of total protein than any other solvent. This can probably be ascribed to the damaged condition of the wheat from which these samples were milled. Flour No. 302 was

musty, of very poor color, and showed abnormally high protein solubility in water. No abnormality was shown by either of these flours when the extraction data obtained with the salt solutions were examined.

When the average per cent of total protein extracted from all the flours by each of the four solvents is considered, it is seen that distilled water removes more protein than either $\frac{N}{2}$ $MgSO_4$ or $\frac{N}{2}$ NaCl. Both these salts must exert a coagulating effect upon some of the flour proteins, although the effect of the latter is relatively slight. With the exception of flours Nos. 302 and 303, $\frac{N}{2}$ KBr extracts more protein from the flours than distilled water. There appears to be a general decrease in per cent of total protein removed with increasing crude flour protein.

The figures in Table V show, that with the exception of the data for the KBr series, the percentage of extracted protein remains practically constant for the different flours with the result that the percentage of non-extracted protein increases as the total protein increases.

TABLE V

COMPARATIVE EXTRACTION DATA FOR EXTRACTED AND NON-EXTRACTED PROTEIN FRACTIONS, COMPUTED AS PER CENT OF FLOUR SAMPLE

Flour number	Crude protein of flour	Non-extracted protein by				Extracted protein by			
		H_2O	$\frac{N}{2}$ $MgSO_4$	$\frac{N}{2}$ NaCl	$\frac{N}{2}$ KBr	H_2O	$\frac{N}{2}$ $MgSO_4$	$\frac{N}{2}$ NaCl	$\frac{N}{2}$ KBr
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
301	9.4	7.5	8.2	7.3	6.3	1.9	1.2	2.1	3.1
302 [1]	10.4	5.9	8.5	7.7	7.6	4.4	1.9	2.7	2.8
303 [1]	11.0	7.8	8.9	8.7	8.2	3.2	2.1	2.3	2.8
304	11.3	8.4	8.9	8.3	7.7	2.9	2.1	2.7	3.3
305	11.7	8.5	9.7	9.4	8.3	3.2	2.0	2.3	3.4
306	12.6	9.5	10.6	10.3	9.0	3.1	2.0	2.3	3.6
307	13.0	10.4	10.9	10.5	9.5	2.5	2.1	2.5	3.5
308	13.3	11.2	11.4	11.2	9.2	2.1	1.9	2.1	4.1
309	13.8	11.1	11.9	11.7	10.0	2.7	1.9	2.1	3.8
310	14.0	11.7	12.3	11.2	9.9	2.3	1.7	2.8	4.1
311	14.7	12.0	12.2	11.9	10.8	2.7	2.5	2.8	3.9
312	15.6	12.9	13.1	13.0	11.9	2.7	2.5	2.6	3.7
313	16.0	13.4	13.3	12.4	10.9	2.6	2.7	3.6	5.1
314	18.2	15 4	16.0	15.3	14.3	2.8	2.2	2.9	3.9
315	20.2	17.6	17.7	16.8	15.8	2.6	2.5	3.4	4.4

[1] Samples milled from musty wheat.

A statistical treatment of the extraction data is shown in Table VI, using the method first employed by Geddes and Goulden (1930) and since used by Harris (1931a). The significance of these correlation coefficients may be judged by comparison with the points of minimum significance according to the number of pairs of observations.

TABLE VI

STATISTICAL CONSTANTS COMPUTED FOR BAKING AND EXTRACTION DATA

H_2O	$\frac{N}{2}$ $MgSO_4$	$\frac{N}{2}$ NaCl	$\frac{N}{2}$ KBr
r_{ae} = +.9630	+.9630	+.9630	+.9630
r_{ad} = −.6887	−.4329	−.6029	−.5808
r_{be} = −.2954	+.6482	+.6376	+.6933
r_{bc} = −.4289	+.5861	+.5784	+.6336
r_{ce} = +.9607	+.9556	+.9554	+.9548
r_{de} = −.7234	−.4359	−.6088	−.4833
${}_b r_{ce}$ = +.9664	+.9331	+.9334	+.9246
${}_c r_{be}$ = +.4651	−.0049	+.0352	+.0384
$R(bc)e$ = +.9693	+.9617	+.9609	+.9616

Value at 5% point for total correlation = +.5139
Value at 5% point for partial correlation = +.5324

Note:

a = crude protein
b = extracted protein
c = non-extracted protein
d = per cent total protein extracted
e = loaf volume (2 mg. $KBrO_3$)

The practical significance of the non-extracted protein is evident, while extracted protein is less useful as a means of predicting loaf volume. There is little evidence of increasing importance of extracted protein in going from H_2O to KBr. There appears to be no increase in significance of per cent of total protein extracted with increasing peptizing ability of the medium. The multiple correlations show no increased information obtained by splitting the protein into the two fractions "b" and "c." These results confirm the earlier findings of Geddes and Goulden (1930) as well as those of the author (1931a), namely, that no information is to be gained by peptization studies over that yielded by a knowledge of the total protein content alone.

Summary

A preliminary baking experiment conducted with four flours of widely different protein contents showed higher loaf volumes when diastatic malt was used with successive increments of 1 mg. of $KBrO_3$ than when the bromate was used without malt.

Using the method which gave the largest loaf volumes more extensive investigation was carried out, using 15 flours from the 1930 Saskatchewan wheat crop. Commercial, experimental, and millstream flours were included in the studies. Samples of flour milled from Marquis and Garnet wheats were present in the series.

Two of the flours studied would be considered rather unsound.

The series of 15 flours was baked, using a basic method, and the basic method modified by the addition of 1% of diastatic malt and 1 to 4 mgs. of $KBrO_3$. The higher protein flours reacted most vigorously to the higher concentrations of $KBrO_3$.

With the higher protein content flours, a progressive increase in loaf volume was noted with increasing protein content for each concentration of bromate up to, and including, 3 mgs. of $KBrO_3$. Correlation constants computed between flour protein and loaf volume obtained by the use of different amounts of $KBrO_3$ in the test bake revealed higher values for the constant when 2 mg. or more of $KBrO_3$ were used. These values did not differ significantly, however, when the Z test for significance was applied.

The proteins of these flours were extracted by H_2O and $\frac{N}{2}$ $MgSO_4$, NaCl and KBr. Distilled water extracted more protein than $\frac{N}{2}$ $MgSO_4$ from 13 flours, and more than NaCl from 7 flours. In the case of the two unsound flours water extracted more protein than $\frac{N}{2}$ KBr.

A statistical treatment of the baking and extraction data showed very high positive significant correlations between nonextracted protein and loaf volume. No very great trend was evident towards increasing importance of extracted protein with increasing peptizing ability of the medium. The constants obtained by splitting the protein into fractions and computing their relationship with loaf volume showed no greater utility than when crude protein alone was considered. These results are in agreement with previous findings.

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A NOTE ON THE USE OF SELENIUM AS A CATALYST IN KJELDAHL DIGESTION WITH NATURAL GAS HEAT

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There are disadvantages to the catalysts commonly used in Kjeldahl digestion. Copper is slow in action necessitating a long digestion; mercury, while rapid in action, requires the use of a precipitant in the later distillation.

Lauro [1] has proposed selenium as a substitute for these catalysts. He reports that selenium shortens the digestion period and eliminates the use of the precipitant in the distillation.

Since shortening the time of Kjeldahl digestion is of major importance to cereal chemists it was thought desirable to compare metallic selenium with metallic copper and mercuric oxide in the digestion of wheat products, using natural gas heat for digestion. For this purpose a series of determinations were made on a high protein flour and a sample of ground bran using 25 cc. sulfuric acid, 12 to 13 grams potassium sulfate, and the catalyst (0.1 gram copper, 0.7 gram mercuric oxide, or 0.1 gram selenium). The digestion time was varied from 30 to 150 minutes using the most intense heat obtainable without allowing the flame to touch the flask above the surface of the liquid, and not permitting the blue cone of the flame to touch the flask. Table I gives the results obtained, each value an average of four determinations.

[1] Lauro, M. F. Use of selenium as catalyst in determination of nitrogen by Kjeldahl method. J. Ind. Eng. Chem. Analytical Edition, 1931, **3**: 401–402.

TABLE I

COMPARISON OF SELENIUM, MERCURIC OXIDE, AND COPPER AS CATALYSTS IN KJELDAHL DIGESTION

Digestion time	Catalyst	Protein in flour (N×5.7)	Protein in bran (N×6.25)
Min.		P.ct.	P.ct.
30	Se	15.47	15.87
30	HgO	15.58	15.89
30	Cu	15.26	15.58
45	Se	15.60	15.95
45	HgO	15.62	15.95
45	Cu	15.44	15.69
60	Se	15.64	15.92
60	HgO	15.64	15.97
60	Cu	15.63	15.92
90	Se	15.65	15.95
90	HgO	15.65	15.94
90	Cu	15.64	15.94
120	Se	15.62	15.89
120	HgO	15.67	15.89
120	Cu	15.64	15.97
150	Se	15.56	15.66
150	HgO	15.64	15.96
150	Cu	15.64	16.00

Under these conditions metallic selenium acted more rapidly than metallic copper, and at about the same rate as mercuric oxide. The digestion of the samples with selenium and with mercuric oxide was almost complete in 30 minutes and was complete in 45 minutes; while the digestion with copper was complete in one hour. It appears that there is greater danger of losing nitrogen by extremely long digestion with selenium than with the other catalysts.

The cost of the catalyst per determination is also of interest especially to those who do a large volume of protein testing. One-tenth gram of metallic selenium powder, the amount used for one determination, costs approximately 0.15 cents as against about 0.48 cents for 0.7 gram of mercuric oxide or about 0.002 cents for 0.1 gram copper.

Selenium also has the advantage over mercury of not requiring a precipitant in distillation.

A METHOD FOR QUICK ASHING OF FLOURS

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The ordinary way of ashing flour is a slow process at best. The fineness of the flour particles together with its low ash content creates a condition wherein oxidation of the last traces of carbon takes place with difficulty. This condition becomes more pronounced as the temperature of ashing increases.

Some years ago in analyzing flour for various bakers in the state of Iowa, the writer made use of a solution of magnesium nitrate to produce a clean white ash. The produced ash was always very satisfactory in appearance and this together with the fact that the ash of flour or wheat as run by slow heating contains probably less than .005% chlorine suggested that possibly nitric acid might be used to complete oxidation after the flour had been partly ashed in a rather hurried way. A study of the effect of HNO_3 as an aid to a more rapid ashing of flour was, therefore, undertaken.

Although we were first interested in devising a method for the quick ashing of whole wheat flour, the investigations finally included ordinary flours. It is in this connection that the method shortly to be given, becomes most helpful.

It was assumed that the slow manner in which some substances ash is due to particles of carbon becoming incased in the flour ash as it forms during ashing. Under such conditions oxygen is excluded as an

TABLE I

INFLUENCE OF HNO_3 AND H_2O ON ASH RESULTS

Flour number	Ash using nitric acid	Ash using water
	P.ct.	P.ct.
4129	1.560	1.545
	1.575	1.580
4166	1.630	1.660
	1.660	1.660
4173	1.760	1.805
	1.810	1.770
4216	1.760	1.750

aid to complete combustion. This assumption was substantiated by the fact that while trying out the action of nitric acid in connection with flour ashing, a similar series of tests were made using distilled water and the results obtained were practically the same as the results obtained with the slow process of ashing or with nitric acid, as can be seen from the data shown in Table I.

As a result of preliminary studies the following method was developed:

Exactly 2 or 3 grams of flour are ashed in a muffle, which is regulated to heat to a noticeable red in about 60 minutes with the door left open. Heating is continued at this adjustment until the color of the oven is slightly above dull red. At this point the ash appears a dirty gray with no noticeable black or charred particles. The crucible with its contents is then removed from the muffle and allowed to cool. This required about 5 minutes. Meanwhile, the current is turned off from the muffle and the door closed. When the crucible has cooled, 10 drops of (1 + 19) solution of nitric acid are added and the moistened ash agitated by gently rotating and warming to loosen all particles from the bottom of the crucible. The crucible is then set on the opened muffle door and the HNO_3 solution allowed to evaporate at a rate which will not permit it to boil. No spattering will take place because of a slight evolution of gas. After the ash has become dry the crucible is placed back in the muffle, the door closed, and the temperature raised

TABLE II

COMPARATIVE RESULTS, SLOW ASHING VERSUS ASHING WITH THE AID OF HNO_3

Flour number	Slow ash method	HNO_3 method	Average of collaborative tests
	P.ct.	P.ct.	P.ct.
4040	1.800	1.810	
	1.830	1.840	
4254	1.765	1.775	
	1.750	1.745	
4253	1.700	1.670	
	1.695	1.690	
4002	0.450	0.445	
	0.440	0.440	
6041	0.487	0.487	
	0.483	0.473	0.476
	0.490	0.480	
6776	0.447	0.443	
	0.440	0.453	0.459
	0.447	0.460	

to the faintest dull red. The resulting ash will be perfectly white and all traces of nitrate are expelled.

Should a slightly pinkish cast exist in any part of the ash after this final heating, it indicates that either the temperature was not sufficiently high or that the heating time was not long enough. Standing in the cooling muffle for any length of time after this does no harm.

In Table II are given some comparative results by the slow way of ashing, and by the more rapid one with nitric acid.

The reported average submitted by 30 members of the St. Louis and Central States section of the A. A. C. C., which membership made ash determinations on samples Nos. 6041 and 6776, was 0.476% and 0.459%, respectively. It should be pointed out, however, that the tests made by this group varied from a maximum of 0.53%, to a minimum of 0.463%, for sample No. 6041; while for sample No. 6776, the maximum ash value reported was 0.486%, the minimum 0.430%.

The results submitted show that the use of dilute nitric acid shortens the period for ashing flours, and makes possible ash results of the same degree of accuracy as the slow burning method. The author has also found it extremely convenient.

Since a great many organic substances when ashed lose the chlorine that they may have originally contained, unless it is bound by some alkaline substance as sodium carbonate, nitric acid can be used as a means of hastening their ashing without danger of obtaining an erroneous ash content.

BULLETIN REVIEW

Protein Tests for Wheat and Oil Tests for Flaxseed and Soybeans, Importance in Production and Marketing. (Miscellaneous Publication 140.) U. S. Department of Agriculture, 45 pp. February, 1932. E. C. Parker, et al.

This report covers studies of protein premiums in the principal grain markets since 1923, the effect of the average protein content of the nation's wheat crops on protein premiums, the existing methods for the determination of protein content, and studies of methods for improving the testing of wheat for protein and improving the marketing practices for merchandising wheat by its protein content. The importance of the Wesson oil test for determining the oil content of flaxseed and soybeans and the importance of oil content as a measure of the commercial value of these commodities is discussed also in this report. The need for oil tests in the merchandizing of soybeans is indicated by this year's export transactions in soybeans through the port of New Orleans, where shippers have been asked to guarantee a minimum oil content of 18 per cent in the deliveries.

Copies of the above publication may be obtained by writing to the Division of Publications, Office of Information, United States Department of Agriculture, Washington, D. C.

ON ROPE CONTROL

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(Received for publication February 15, 1932)

Introduction

In our earlier articles on this subject we reported a method for recognizing ropiness of bread in its very early stages, when such ropiness could not be detected by the ordinary methods. During the year 1931 we examined 530 loaves of bread for rope. These rope tests represent 57 bakeries throughout the east (several in the middle west and south) belonging to 11 different organizations. Out of the 530 rope examinations, 63 were distinctly positive; 122 on the border line; and 345 negative. The surprisingly high percentage of positive and border line cases, together 35% of the total examined, is undoubtedly due to the fact that bakers seek a cure when in trouble rather than prophylactic measures when all is well. In other words, most of the samples examined represent cases of suspected rope.

By border line cases we mean breads showing a figure of infection so slight that there will not develop an offensive odor or any other outward signs of ropiness on examination after three days room storage and fairly high humidity. Experience has taught us that from a merchandising point of view this condition is not to be ignored. There is a certain amount of flavor destruction taking place just prior to the development of the generally known symptoms of ropiness. This loss of flavor unquestionably reflects itself in sales, sooner or later, but will not be associated in the baker's mind with ropiness and he will, therefore, frequently take no special steps to protect himself against it. For this reason it seemed, to us, that this very slight "border line" ropiness deserves special attention. We have, therefore, during the past year directed our attention toward increasing the sensitiveness of our catalase method. We have studied the optimum conditions of pH, H_2O_2 concentration and incubation temperature. We have also studied the relationship existing between the amount of ropy material used and the catalase reading. This was done to enable us to compare results of experiments in which different amounts of ropy material were used, the amount of material used in each case depending, of course, on its degree of activity. In this way a more sensitive modification of the method was evolved.

Material Used

We found it easy to prepare very active catalase material in which the activity was mainly or entirely due to B. mesentericus and allied organisms. In one of our regular test bakes a very small amount, about 0.1 gm., of badly infected bread was stirred into the water used. The total amount of water used in a test bake is close to one pound. After baking, the bread was incubated for three days at 40° C. The crumb which showed the extreme stages of rope disintegration was dried in a dessicator and ground until four-fifths of it went through a 70 mesh sieve. This powder was used for all of our rope catalase experiments.

In order to gain a conception of the degree of catalase activity in this material, one of our students, Miss Lefkowitz, compared it with a number of plant and animal tissues as well as some ordinary foods. The results are shown in Table I.

TABLE I

COMPARISON OF THE CATALASE ACTIVITY OF CERTAIN ANIMAL AND PLANT TISSUES AS WELL AS SOME ORDINARY FOODS

Concentration of H_2O_2 in mixture $-0.2N$			
Substance	Catalase units [1]	Substance	Catalase units [1]
Rope Catalase preparation	32920.0	Egg Yolk (fresh)	0.0
Wheat flour (short patent)	226.2	Egg Yolk (24 days)	54.6
Wheat germ	13237.7	Milk (fresh pasteurized)	3.2
Potato (Irish, pulp)	1866.7	Milk (pasteurized 3 days old)	15.2
Potato (Irish, peeling)	2342.3	Beef (muscle)	2662.0
Potato (sweet, pulp)	2310.7	Beef (fat)	4940.5
Potato (sweet, peeling)	1755.6	Lamb (heart)	3177.0
Carrot (pulp)	4365.9	Lamb (kidney)	30312.5
Lettuce	2617.7	Lamb (lung)	21555.0
Spinach	5017.5	Rabbit (muscle)	5444.0
Egg white (fresh)	636.2	Rabbit (lung)	14492.5
Egg white (24 days)	17.1	Rabbit (kidney)	58180.0
		Blood (ox, oxalated)	197785.0

[1] Based on oxygen pressure produced by one gram of material in five minutes.

Of all the materials used, only two, rabbit kidney and ox blood, showed greater activity than the rope catalase. We believe that the very high catalase activity of the kidney is largely due to the blood contained therein.

Effect of Hydrogen Peroxide Concentration

In these experiments the catalase containing preparation described above was used by suspending 1 gm. of the mixture in 100 cc. of distilled water. Suitable amounts of this suspension were pipetted with a rapidly delivering pipette into a Bunzell Catalase Apparatus (1930).

Three concentrations of hydrogen peroxide were procured—3% (10 vol.), 5% (17 vol.), and 30% (100 vol.). The 3% and 5% were preserved by 3/16 of a grain of acetanilid per ounce of hydrogen peroxide. The 30% was preserved by 10 grains of cinchonidine sulphate per gallon.[1] All the hydrogen peroxide solutions were standardized by the well known potassium permanganate method and the normality of the ultimate mixture was calculated.

Table II shows the effect of varying concentrations of hydrogen peroxide upon the catalase units produced in five minutes by 1 gm. of the catalase containing preparation.

TABLE II

EFFECT OF VARYING CONCENTRATIONS OF HYDROGEN PEROXIDE UPON CATALASE ACTIVITY. UNITS PRODUCED IN FIVE MINUTES BY ONE GRAM OF CATALASE CONTAINING PREPARATION

Normality of H_2O_2 in final mixture	Catalase units	Normality of H_2O_2 in final mixture	Catalase units
2.0470	41370.0	0.7136	99200.0
2.0242	35970.0	0.6775	118080.0
1.7000	44080.0	0.6713	107460.0
1.3990	73960.0	0.6713	110200.0
1.3010	70260.0	0.6587	110200.0
1.2253	79580.0	0.6186	104280.0
1.0944	82340.0	0.6157	109760.0
0.9979	104720.0	0.5918	132760.0
0.9803	98800.0	0.5678	98800.0
0.8099	101520.0	0.5559	104280.0
0.7890	104280.0	0.5376	96040.0
0.7818	98800.0	0.4722	82320.0
0.3617	102740.0	0.3228	71360.0
0.3168	88160.0	0.3052	96000.0
0.2042	54400.0	0.0940	46260.0
0.0506	36060.0	0.0244	21110.0
0.0117	11000.0		

In Figure 1, curve A, these results are shown graphically. Curve B shows the oxygen liberated, calculated in catalase units, by the varying concentrations of hydrogen peroxide when shaken in the catalase apparatus without any catalase containing material.

There appears to be a direct proportionality between the rate of hydrogen peroxide decomposition and the concentration of the hydrogen peroxide used until a concentration of 0.6N is reached. In concentrations above this the rate of decomposition is slowed down indicating destruction of the catalase by the hydrogen peroxide.

Reaction of the Medium

Experiments on relation of hydrogen-ion concentration and catalase activity were carried out by one of our students, Miss Duer. A series

[1] The hydrogen peroxide solutions used throughout this investigation were furnished by Mr. Jewell, of the Schuylkill Chemical Company, and we express our appreciation of his courtesy.

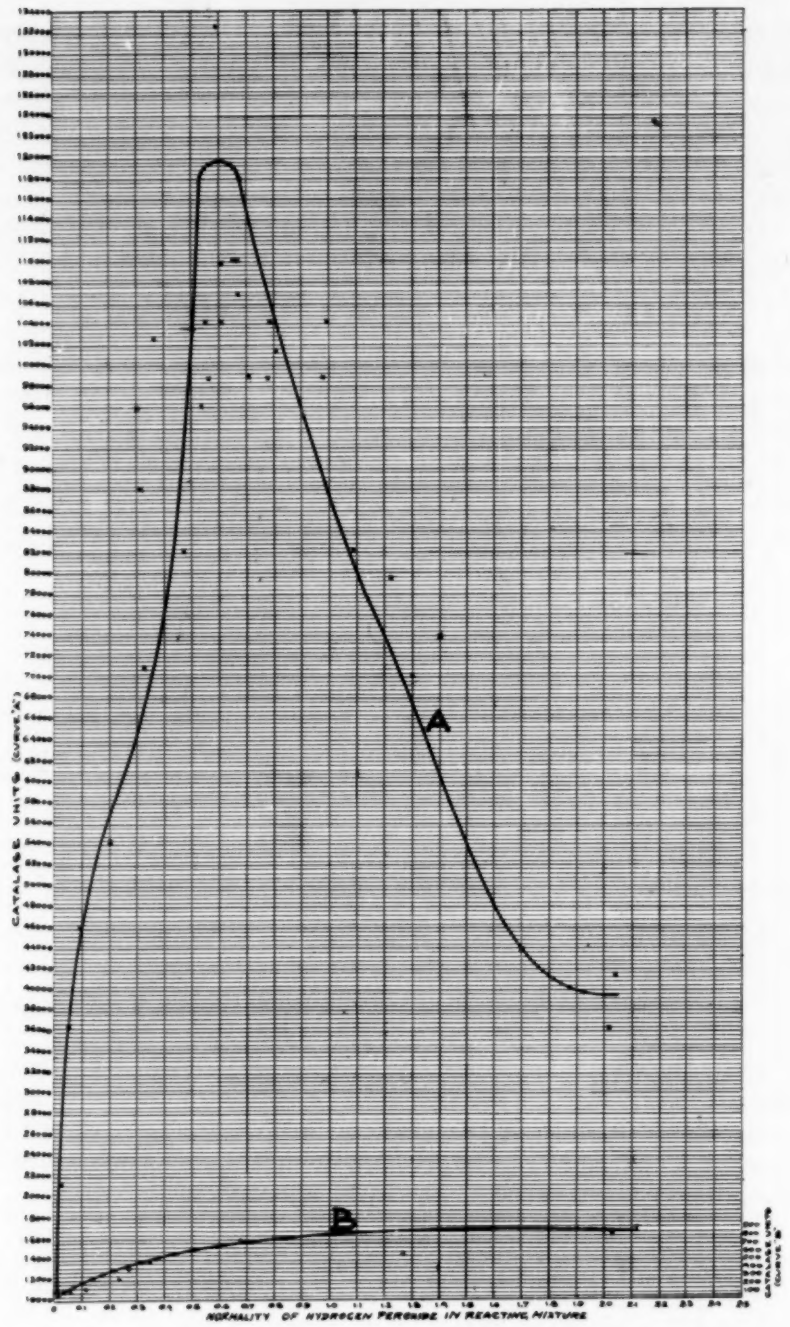

Fig. 1. Relationship between hydrogen peroxide concentration and catalase activity.

of determinations was run using the B. mesentericus preparation, an ultimate hydrogen peroxide concentration of 0.2N, a mean temperature of 25° C., and varying pH. The varying hydrogen-ion concentrations were obtained by replacing some of the water ordinarily used with 0.1055N acetic acid and 0.1010N sodium hydroxide. The reactions of the mixtures were determined as accurately as possible by the use of a Hellige Klett Comparator and the following indicators: Thymol Blue, Phenol Red, Bromthymol Blue, Chlorphenol Red, and Bromcresol Green. The results are shown in Table III.

TABLE III

RELATION BETWEEN HYDROGEN-ION CONCENTRATION AND CATALASE ACTIVITY

pH	Catalase units for 1 gm. of B. mesentericus preparation—5 minutes
3.8	5530.0
3.9	8300.0
4.0	7022.5
4.5	32935.0
8.3	39270.0
9.1	50292.5
9.2	55325.0
9.4	46050.0
9.5	31062.5

From these experiments it is evident that 9.2 is the optimum pH for catalase activity when the ultimate hydrogen peroxide concentration is 0.2N. It would therefore seem that the activity of the 0.6N reacting mixture might be increased by adjusting it to the pH 9.2. With this in mind several series of experiments were run.

(*a*) An approximately 6N hydrogen peroxide solution was prepared from 100 volume hydrogen peroxide, 0.1N sodium hydroxide, and distilled water. It was found that, to obtain an ultimate pH of 9, 50 cc. of 0.1 NaOH were required to make 100 cc. of the hydrogen peroxide mixture. With this amount of alkali the hydrogen peroxide was unstable, turning yellow and bubbling freely. In four days time the solution changed from 5.8478N to 3.900N when kept at room temperature, and from 5.7942N to 5.2040N when kept in the ice box.

(*b*) We then tried adding the required amount of 0.1N NaOH to the mixture of catalase material and water in the main bulb of the catalase apparatus. That the catalase activity was destroyed by the high alkalinity before the hydrogen peroxide could be added, is shown by a drop from 107460.0 to 75720.0 catalase units.

(*c*) Several buffer mixtures maintaining a pH of 9 were used including those suggested by Sörensen, Palitzsch, and Clark and Lubs.

These solutions when mixed with the hydrogen peroxide all resulted in a measurable diminution in the strength of the hydrogen peroxide. The Clark and Lubs buffer (boric acid and sodium hydrate) caused a change from 5.995N to 5.794N on ice in a four-week period, and from 6.128N to 4.056N at room temperature in four weeks. While this change was slow enough to permit the use of this buffer mixture, the catalase activity was destroyed under its influence. At the highest pH obtainable with this buffer, i.e., pH of 8.5, the catalase activity of the B. mesentericus preparation was 71900.0 units as compared with 107460.0 units, when no buffer was used.

An ammonium chloride-ammonium hydroxide mixture was tried as buffer but the H_2O_2 normality of the mixture dropped from 6.0202 to 5.1062 in two hours.

(*d*) Hydrogen peroxide is fairly stable in the presence of sodium silicate. Mixtures were made containing varying amounts of 40% sodium silicate solution. Results obtained were not satisfactory. The mixture containing sufficient sodium silicate to give a pH of 9 did not show as high catalase activity as when hydrogen peroxide alone was used.

A pH of 9 may be more desirable if we could find the proper buffer, i.e., something that would give a pH of 9 without destroying either the hydrogen peroxide or the catalase. So far we have been unable to find such a buffer.

Amount of Catalase Material

Curve A, Figure 2 shows the millimeters of oxygen liberated at 25° C. by varying amounts of catalase containing material. As shown in Table IV the catalase units as calculated from these readings for 1 gm. of material are nearly constant.[2]

It is evident that in all but the first two measurements, the activity is directly proportional to the amount of material used. The deviations from this rule in the first two cases is probably due to adsorption of some of the oxygen liberated by the colloidal matter present.

It seemed desirable to also study the relation between the amount of material used and catalase activity in less active preparations. For this purpose a mixture of 90% flour and 10% B. mesentericus preparation was made. Results obtained from this mixture are recorded in curve B, Figure 2, and Table V.

As shown in curve B, Figure 2, the relationship here is also represented fairly well by a straight line but is not one of direct proportionality. This deviation is probably also due to adsorption of some of

[2] A fresh rope catalase preparation different from the one used in experiments recorded in Table I, was used for these experiments.

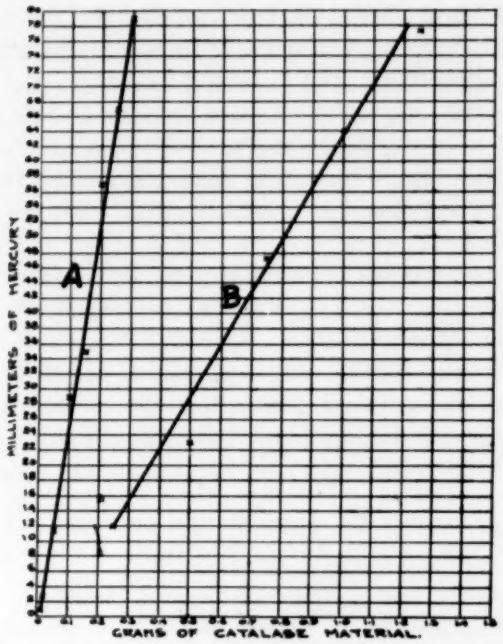

Fig. 2. Relationship between amount of catalase containing material and catalase activity.

TABLE IV

RELATION BETWEEN AMOUNT OF CATALASE CONTAINING MATERIAL AND OXYGEN LIBERATION

Amount of B. mesentericus preparation used	mm. of O_2	Catalase units calculated on 1 gm. 25° C. 0.2N H_2O_2
0.01	1.0	6425.0
.02	2.5	8595.0
.05	11.5	15850.0
.10	29.0	19992.5
.15	35.0	15914.2
.20	57.0	19673.7
.25	67.0	18442.0
.30	79.0	17917.3

TABLE V

RELATION BETWEEN AMOUNT OF CATALASE CONTAINING MATERIAL AND CATALASE ACTIVITY WITH LESS ACTIVITY PREPARATIONS

Amount of mixture used (10% B. mesentericus preparation and 90% flour)	mm. of O_2	Catalase units calculated on 1 gm. of mixture 25° C.–0.2N H_2O_2
0.25	12.0	3316.0
.50	23.0	3159.5
.75	47.5	4175.7
1.00	64.0	4846.1
1.25	77.0	6639.5

the oxygen by the colloidal matter present and is correspondingly greater because of the larger amount of such colloidal matter, owing to the admixture of the flour.

To determine the degree of infection of a loaf of bread in the shortest possible time, it was necessary to find the optimum temperature for incubating the loaf. A sample bake was made, therefore, using 0.60 gms. of infected flour per pound of flour. Six one-pound loaves baked from this infected flour, were cooled at room temperature for one hour and then wrapped in paraffine paper. Loaf No. 1 was allowed to remain at laboratory temperature (approximately 20° C.), loaf No. 2 placed in an incubator at 30° C., loaf No. 3 at 40° C., loaf No. 4 at 45° C., loaf No. 5 at 50° C., and loaf No. 6 at 60° C. At the end of sixteen hours the catalase activity of the crumb taken from the center of the loaf was determined. Table VI shows the results.

TABLE VI

RELATION BETWEEN TIME, TEMPERATURE, AND CATALASE ACTIVITY

Loaf	1	2	3	4	5	6
Temp. of incubation	20° C.	30° C.	40° C.	45° C.	50° C.	60° C.
Time of incubation	16 hrs.	16 hrs.	16 hrs.	16 hrs.	16 hrs.	16 hrs.
Conc. of H_2O_2 used	6N	6N	6N	6N	6N	6N
Wt. of inf. bread used	10 g.	.5 g.	.5 g.	.5 g.	.5 g.	10 g.
Reading in mm.	3.5	22.0	33.5	32.0	10.0	7.0
Corrected for H_2O_2 decomposition	1.5	20.0	31.5	30.0	8.0	5.0
Activity in units	10	2794	4357	4172	1106	35

It is evident that the best results are obtained by maintaining the temperature of incubation as near 40° C. as practicable. This is lower than the supposed optimum incubation temperature referred to in our former paper.

Conclusions

Method for determining degree of infection of bread by catalase method becomes more sensitive when 6N H_2O_2 is used and incubation is carried out at 40° C. With these modifications of the original method it is possible to complete a determination within sixteen and a half hours after receipt of sample.

Literature Cited

Bunzell, H. H.
1930 A simple apparatus for measuring catalase activity in plant and animal tissues. Science, **72**: 1872: 505–506.
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1930 A method for testing for ropiness of bread. Cereal Chem. **7**: 465–472.

A NOTE ON THE VALUE OF THE VISCOSITY TEST FOR DETERMINING SOME OF THE PROPERTIES OF CAKE AND PASTRY FLOURS [1]

GEO. L. ALEXANDER
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(Received for publication January 8, 1932)

A great amount of work was done some years ago to popularize the use of the viscosity test in estimating the baking quality of bread flours. It was found, however, that viscosity tests could not be made to consistently predict baking performances, and so work along this line has apparently come to a standstill. Such viscosity tests are made on a flour suspension or batter-like emulsion, which differs considerably in physical nature from the dough form in which bread flour is handled.

In all cake batters, however, in which flour is used to give body and coherence, and later to form a solid structure supporting the other ingredients in the final product, the flour gluten behaves much as it does in the viscosity test. For this reason, the viscosity determinations have been found to be quite valuable as a supplementary test in our laboratory, in determining the baking possibilities of cake and pastry flours.

An arbitrary method is used, and all conditions are maintained as uniform as possible, so that all tests are comparative. As both the quantity and quality of gluten affect the results, an amount of flour is used in each test so that it contains exactly two grams of protein in order to eliminate the quantity factor. Use is made of MacMichael viscosimeter, with a disc bob and a No. 28 wire. The flour is left in suspension with 100 cc.'s of distilled water for one hour; then 5 cc.'s of N/1 lactic acid is added, the mixture shaken lightly. After five minutes this emulsion is poured into the viscosimeter bowl, and the reading taken at 80°–82° F. The speed of viscosimeter bowl is 25 r. p. m.

From the tests that have been made, three zones of cake and pastry flour performance have been worked out, bearing in mind the protein and ash content of the flour under consideration. The lower zone, up to a certain limit, indicates, according to our experience, a flour suited for pastries, pie crust, cookies, fried cakes, and other products of a nature requiring a short tender gluten with low shortening and sugar tolerance, which spreads or flattens in the oven instead of coming up round.

[1] From the report of the mid-year meeting of the Committee on the Testing of Soft Wheat Flours.

The second or intermediate zone of readings indicates a flour of somewhat greater sugar and shortening requirements, and which can be used for either pastry products or the so-called light cakes. Other things being equal, such a flour will not give quite the volume in the so-called "light" cakes as will the stronger type of cake flours, nor will it carry as much weight of other ingredients without falling or shrinking. However, the crumb will be more tender and finely grained, and the keeping quality of the cake will be better. Flour of this type does well for those who want a flour for making all types of baking powder cakes and pastries.

The third zone of viscosity readings takes in flours which have little tendency to make cakes that spread in the oven, unless large amounts of ingredients known to produce this condition are added to the batter. This zone included flours of the greatest sugar and shortening tolerance and milk absorption, and which produce the greatest cake volume and the firmest cake structure. The keeping quality is generally lowest in this type of cakes, and the crumb is not as tender.

Under the conditions of testing described above, the zones spoken of are as follows:

1. 30 to 50 degrees MacMichael
2. 51 to 65 " "
3. 66 to 85 " "

Flours are rarely found testing below 30 degrees which are suitable in other respects for making good pastry. Flours testing higher than 85 degrees seem to meet with trouble in both the home and in shop baking because of excessive gluten toughness. However, such flours are very well suited for biscuits and some types of fruit and pound cake and for home bakers who like soft wheat flours for bread.

All the above statements have been checked repeatedly through observation of the work of the commercial bakers. The viscosity test is used regularly in our laboratory, and we find it useful for making a preliminary survey of the flour prior to baking. From the viscosity test it is found that a very good picture of the gluten characteristics of the flour can be obtained, one which the baking test bears out. No difficulty is experienced in obtaining check results within 2 or 3 degrees MacMichael at most. The test is regarded as just as valuable, if not more valuable, than the ash test.

In conclusion, in relating our experiences with the viscosity test we do not want to be placed in the position of defending or claiming that the test is the long sought "tell-all test." In common with all other analytical and physical testing methods, the viscosity test requires some experience and the proper interpretation.

BOOK REVIEWS

Introduction to Agricultural Biochemistry.—By R. Adams Dutcher and Dennis E. Haley. John Wiley and Sons, Inc., New York, 1932. x + 484 pp., 98 figs., 15 x 23 cm. Price $4.50.

" The present volume is an outgrowth of lectures presented to agricultural students over a period of nearly twenty years. The book is designed for those students who have had preliminary training in inorganic and organic chemistry."

The book contains 31 chapters, distributed through three sections.

SECTION I, " General and Introductory " covering 112 pages, contains an introductory chapter of an historical nature in which an outline is given of the development of agricultural chemistry and of discoveries and men who have advanced agricultural science. This chapter is followed by others on " The chemistry of living matter," " The carbohydrates," " The fats and related compounds," " The proteins," " The physical state of matter (including colloids)," and " Enzymes." The treatment of all of these topics is necessarily brief, due to space limitations and also to the fact that the organic chemistry in this section is designed merely to supplement the previous training which the student has already had in a course of organic chemistry. In general, however, this section includes the essentials which, with the supplementary reading which is noted, will provide the student with an adequate background for the more " agricultural " or biological sections which follow.

SECTION II is devoted to " The plant " and includes chapters on " Seed germination," " The soil," " Soil acidity," " Farm manure," " Fertilizers," " The atmosphere," " Insecticides, fungicides and related materials," " Absorption of mineral materials by plants," " Assimilation of mineral nutrients by plants," " The plant carbohydrates," " The plant lipoids," " The vegetable proteins and related compounds," and " Respiration."

SECTION III deals with " The animal " and covers " Foods and feeding stuffs," " Digestion of food," " The body tissues," " Metabolic changes in tissues," " Energy metabolism," " Biological response to foods," " Protein quality," " Vitamin A," " Vitamin B complex (B and G)," " Vitamin C," " Vitamin D and ultra-violet light," and " Vitamin E." A subject index closes the volume.

The book is relatively free from typographical errors; most of those which do occur are obvious slips in proof reading, e.g., formula on pp. 49 and 55. The reviewer does not agree with the formula of muscarine on p. 70. The toxin of *Amanita muscaria* appears to be much more complex than is expressed by the formula of β-tri-methyl ammonium hydroxide acetaldehyde. The statement on p. 79 that protein hydrolysis is carried out by boiling with 10% sulfuric acid, or 30% hydrochloric acid, may cause confusion. The concentrations usually employed are 25% H_2SO_4 (by weight) and 20% (constant boiling) HCl. Using 30% HCl would fill the laboratory with fumes of the gaseous HCl. On p. 82 *hydroxyglutamic acid* should have been included in the list of amino acids, and the sulfur amino acid of " unknown constitution " is " methionine " having the formula—

$$CH_3—S—CH_2—CH_2—CH(NH_2)—COOH.$$

The reviewer questions the wisdom of referring to the peptic digestion of coagulated egg white (p. 99) as an example of " peptization " in the colloid sense since enzymatic hydrolysis involves much more than gel→sol transformation.

This book is a long step forward in texts dealing with Agricultural Chemistry and deserves to be widely adopted for use in Agricultural College classes. The reviewer believes it to be by far the best text available for such courses.

It is very readable and contains an enormous amount of fundamental information. The information is exceedingly condensed,—so much so that in the reading the reviewer often found himself wishing for a greater elaboration of the subject matter. Probably, however, this condensation will serve two very useful purposes, (*a*) it permits the instructor to elaborate in the lectures without unnecessary duplica-

tion of text material, and (*b*) it forces the student into the library and supplementary references (which are provided), and this unquestionably is a valuable educational technic.

Cereal chemists will find much of interest in the book, particularly in "The plant" section. The reviewer feels that the chapter on respiration is particularly outstanding, since it includes a critical summary of the newer theories.

Those cereal chemists, who are more or less isolated in mill or technological laboratories, can well afford to browse through this volume for they will unquestionably find much which will be of use to them.

ROSS AIKEN GORTNER

Colloid Aspects of Food Chemistry and Technology. By William Clayton. 571 pages, 64 illustrations. P. Blakiston's Son & Co., Inc., Philadelphia, 1932.

The author, who is chief chemist and bacteriologist of one of the largest and best known of the British food houses, in the preface of his book calls attention to the lack of surveys of the physico-chemical aspects of food chemistry which come within the range of modern colloid chemistry. This book is designed to fill this gap. After a brief discussion of the scope of colloid chemistry he launches at once into a consideration of colloid phenomena and problems as related to such materials as agar-agar and gums, proteins (with a special chapter on gelatin), cereals, milk and milk products, sugar, jellies, jams, marmalades, beer, wines, and water. Special treatment is accorded the general subjects of emulsions, and of the freezing and thawing of colloid systems.

Readers of this journal will doubtless be particularly interested in Chapter V, "Colloids in Cereal Chemistry" (pages 115–164). This chapter includes a consideration of the colloid chemistry of the starches, pH and buffer value of flour, viscosity, proteins and protein peptization, flour strength, dough tenacity, and staling of bread.

This constitutes a fairly adequate outline, and Clayton has crowded a considerable number of facts into the limited space here afforded. As in all such excursions into a new field of development, it has proven difficult to distinguish between pūrely chemical, and colloidal aspects. This is not serious, of course, and particularly in the instance of as complex a situation as is encountered in bread dough.

There are instances, however, when a little more expansion to include other viewpoints would prove useful in the end to students of this subject. Thus Kondo and Hayashi's values for the iso-electric point of glutenin might have been included, with the values reported by Tague. Corresponding values as reported for gliadin might be of interest likewise. Haworth's views respecting the chemical constitution of starch should certainly find a place with those of Irvine. In the discussion of viscosity of flour suspensions (pp. 140–148), the excellent work of Coleman, Dixon and Fellows, and of Swanson merits some attention. Bungenberg de Jong and Klaar's consideration of the colloid chemistry of gluten might have been added; also the results of the extensive work of Haugaard and Johnson, at the Carlsberg Laboratory, on the thermal fractionation of gliadin.

In discussing the preparation of glutenin (p. 147) no reference is made to the important suggestion made by Blish respecting the desirability of avoiding the treatment with NaOH in order to insure that part or all of the material is not racemized or otherwise altered by the alkali.

Swanson's essay on the colloidal properties of dough deserves the passing mention that it receives, but no treatment of this subject is quite complete without reference to Moh's "Neu Erkenntnise" which passed through its third edition last year.

The brief discussion of mechanical measurements of dough tenacity is doubtless quite appropriate, but should not have been confined to a mention of the Chopin device. This section, to be complete, should mention the pioneer work of Rejto, and later developments by Hankoczy, Buhler, Brabender, Bailey and others. In fact the consideration of dough as a *plastic* material is limited in this text.

Perhaps the most conspicuous omission in the reviewer's opinion is the lack of mention of the role of lipoids, and particularly of the phospholipins in determining the colloidal behavior of dough. On this side of the Atlantic at least the possible significance of these substances is being stressed more and more. Certainly they cannot be dismissed from consideration as yet. Certain recent applications of egg and soy lecithin to emulsions used in bread and cakes might also be added to the section on page 200.

The reviewer does not wish to close with criticisms, however. As stated in one

of the foregoing paragraphs, Clayton has assembled a great number of useful facts in a logical arrangement. Any food chemist who has not engaged in colloid research can hardly fail to have his reasoning influenced and guided by reading this book.

• C. H. BAILEY.

Das Getreidekorn, by J. F. Hoffmann and K. Mohs. Verlag Paul Parey, Berlin, 1931. 384 pages, 199 cuts. Price R.M. 26.

This work is to be published in two volumes, of which the above is Volume I. The book is a revision of Hoffmann's book of the same name published in 1911. This new edition is organized into three sections and is chiefly the work of K. Mohs, who wrote section two; with the assistance of J. K. Seidel, who prepared section one; and G. Brüchner, who prepared section three.

Section one, "The Storage of Cereals," comprises 105 pages, and discusses the handling of grain in storage; the conditions which hasten or retard respiration of stored grain; the relation between moisture content, viability, number of acid forming bacteria, and the methods of keeping grain in good condition (*a*) by exclusion of oxygen, (*b*) through low temperature, (*c*) by drying, and (*d*) by the destruction of insects either by chemical, physical, or mechanical means. The various kinds of storage are discussed, for example, in sacks, in open and in closed storage bins, as well as the mechanical behavior of grain in storage.

Section two, "The Drying of Cereals," is particularly well illustrated to show the different systems of drying. Among the many driers mentioned and described, are the following from the United States: Hess, Hetherington, S. Howes, Ellis, E. F. Mead, MacDaniel, Morris, and Armour. The various systems for drying germinated barley (malt) are also described, as well as the methods of calculating the cost of drying. This section comprises 115 pages.

Section three, The Grading of Cereals, is the one of most interest to the cereal chemist, as it relates to the grading or valuation of cereals. Among the subjects discussed are (1) sampling; (2) the determination of the outward characteristics of grain, such as (*a*) odor, (*b*) color, including mealiness and flintiness, (*c*) uniformity of size, (*d*) amount of husk, (*e*) weight per volume, (*f*) specific gravity, (*g*) weight per 1000 kernels, and (*h*) purity. Some 45 pages are devoted to these items and yet nowhere is there to be found any description of the many splendid and most useful apparatus devised by scientists of the U. S. Bureau of Agricultural Economics, and which are used so extensively by grain grading laboratories in this country. The illustrations are almost wholly of apparatus of German make. The official United States system of grain standardization receives but scant mention, for example, when the subject of purity is discussed. Later, the Brown-Duvel apparatus is illustrated.

The chemical methods described for grading grain include moisture, viability, protein, feed value, and determination of soundness by the Toxamin test. The most important of these determinations is that of moisture. For this purpose, the old-fashioned air oven is described and illustrated; likewise the method of Hoffmann, which was later elaborated, simplified, and made practicable by Brown and Duvel. The new quick method for the determination of moisture which depends upon the dielectrical constant of grain, is cursorily mentioned.

A small table lists the average moisture, ash, fiber, fat, protein, and nitrogen free extract content of the common cereals; and another table shows their digestibility coefficient and starch values.

Considerable space (some 30 pages) is devoted to a description of the diseases affecting cereals, and the insects and weeds which infest them. Most of the material appearing in this section is the same as that found in the 1911 edition, although it has been considerably rearranged and an appreciable amount of new matter inserted.

Sixty pages are devoted to a description of wheat and other grains, their importance and characteristics, their origin and classes. After describing these features as they relate to barley, additional information regarding the valuation or scoring of barley is given, such as, for example, the effect of protein, hardness and uniformity of kernel, etc. The data included in tabular form, in this connection, are the same as those found in the first edition. The chapter on rice includes a description of the principal world rices and their relative commercial value.

Throughout this whole book, little attention appears to have been given to information found in sources other than German. The extensive researches of the scientists of the United States Department of Agriculture, as well as numerous pertinent papers published in CEREAL CHEMISTRY and in American trade journals, have

been almost completely overlooked. The same applies to work originating or published in France, Italy, England, etc. It would seem that a work of such pretentions would be far more valuable if greater recognition had been given to foreign investigators by more frequent reference to their work.

This first volume contains no bibliography, yet this book does contain considerable general information of real value and will no doubt be found useful to elevator owners, grain driers, grain dealers, and brewers, as well as to students of agriculture.

J. A. LECLERC.

Alcoholic Fermentation. Fourth edition. By A. Harden. 237 pages. Monographs on Biochemistry. Longmans, Green & Co., London and New York. 1932.

The great amount of work done on alcoholic fermentation makes this critical review of the literature very welcome, written, as it is, by an authority on the subject. Besides the chapter headings, only a few of the sub-titles can be mentioned here:

I Historical introduction.
II Zymase and its properties. (Alcoholic fermentation by yeast-juice.)
III Function of phosphates. (Preparation of hexosephosphate. Equation of alcoholic fermentation.)
IV Co-zymase. (Detection and Estimation. Factor "Z.")
V Carboxylase and Carboligase. (Chemistry of the fermentation of pyruvic acid.)
VI Reducing enzyme of yeast. (Dismutation by yeast.)
VII Chemical changes in fermentation. (Lactic acid theory. Pyruvic acid theory. Formic acid theory. Neuberg's fixation theory. Fermentation of glycogen.)
VIII Action of some inhibiting and accelerating agents. (Effect of—aldehydes, arsenates, arsenites, sodium fluoride. Period of induction.)
IX By-products of alcoholic fermentation.
X Mechanism of fermentation. (Fermentation in the yeast cell.)

One of the valuable features of the book is the bibliography containing over 600 references.

Most of the work described has been done with yeast preparations, which do not always act in the same manner as the living cells normally used in baking. Cereal chemists will find it regrettable that not more mention has been made of maltose.

Nevertheless, the book, which is very well printed, gives the reader a clear idea of the present state of knowledge on the complicated subject of alcoholic fermentation.

E. Ziegler.

Mehlchemie. Third edition. By Prof. K. Mohs. 172 pages, 24 illustrations. Verlag Steinkopff, Dresden, 1931. Price R. M. 8 ($2.00).

In this new edition, Dr. Mohs, who is Director of the State Milling Institute, in Berlin, has maintained the same chapters as noted in Cereal Chemistry *6*: 248, where the second edition was reviewed.

The statement that yeast contains diastase has been avoided this time, except in one case (p. 61). Reference has been made to articles by Katz (1925) on the staleness of bread and an interesting X-ray diagram of gluten has been added to the illustrations. Otherwise only minor changes have been made in the text.

The book still remains one of the best publications on dealing with most of the important problems in a simple way.

E. ZIEGLER.